Experimental Studies of Metallic Hydrogen at Very High Pressures

Isaac F. Silvera

Harvard University
Department of Physics
Cambridge MA 02138

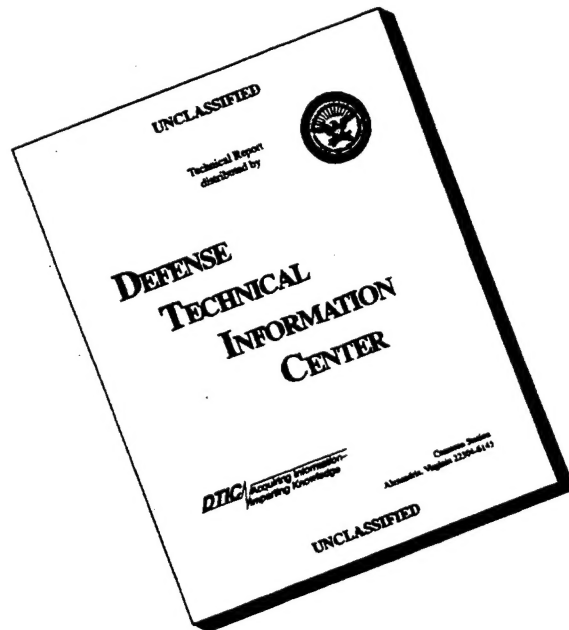January 1996

Final Report   **19960305 088**

PHILLIPS LABORATORY
Propulsion Directorate
AIR FORCE MATERIEL COMMAND
EDWARDS AIR FORCE BASE CA 93524-5000

DTIC QUALITY INSPECTED 1

DISCLAIMER NOTICE

UNCLASSIFIED

Technical Report
distributed by

**DEFENSE
TECHNICAL
INFORMATION
CENTER**

DTIC Acquiring Information·
Imparting Knowledge

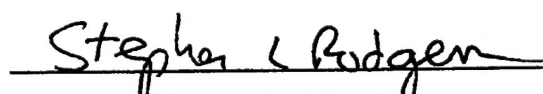Cameron Station
Alexandria, Virginia 22304-6145

UNCLASSIFIED

THIS DOCUMENT IS BEST
QUALITY AVAILABLE. THE
COPY FURNISHED TO DTIC
CONTAINED A SIGNIFICANT
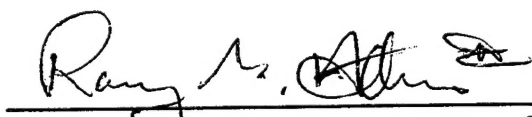NUMBER OF PAGES WHICH DO
NOT REPRODUCE LEGIBLY.

FOREWORD

This report was prepared by Harvard University, Department of Physics, Cambridge, MA 02138, under contract F29601-92-K-0019, for Operating Location AC, Phillips Laboratory, Edwards AFB CA 93524-7048. The Project Manager for Phillips Laboratory was Patrick G. Carrick.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the SF Form 298.

PATRICK G. CARRICK
Project Manager

STEPHEN L. RODGERS
Director
Propulsion Sciences Division

RANNEY G. ADAMS, III
Public Affairs Director

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions searching existing data sources gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0740-0188), Washington DC 20503,

1. AGENCY USE ONLY (LEAVE BLANK	2. REPORT DATE January 1996	3. REPORT TYPE AND DATES COVERED Final Report

4. TITLE AND SUBTITLE

Experimental Studies of Metallic Hydrogen at Very High Pressures

6. AUTHOR(S)

Isaac F. Silvera

5. FUNDING NUMBERS

C: F29601-92-K-0019

PE: 65502F

PR: 3058

TA: 00EW

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Harvard University
Department of Physics
Cambridge MA 02138

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Phillips Laboratory
OLAC PL/RKS
10 E. Saturn Blvd.
Edwards AFB CA 93524-7680

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

PL-TR-95-3030

11. SUPPLEMENTARY NOTES

COSATI CODE(S):   2109; 0702; 0704

12a. DISTRIBUTION/AVAILABILITY STATEMENT	12b. DISTRIBUTION CODE
Approved for public release; distribution is unlimited	A

13. ABSTRACT (MAXIMUM 200 WORDS)

Research to understand and produce metallic hydrogen in the laboratory is described. Metallic hydrogen is predicted to be the most powerful chemical fuel for rocket propulsion, capable of single-stage orbital entry. Solid molecular hydrogen is predicted to transform to the metallic molecular and then metallic atomic phases at megabar pressures. Samples have been pressurized to greater than 2 megabar and studied by spectroscopic and other techniques. A number of new phases have been found and studied in hydrogens (hydrogen and its isotopes, deuterium and hydrogen deuteride), but none have been identified as the metallic phase. Methods of IR spectroscopy have been developed to study the hydrogens and new lattice modes and vibrons have been observed. Group theoretical techniques have been used in efforts to identify the structures of the new phases and many of the structures used by theorists have been eliminated from consideration. Measurements in the extended IR of absorption to demonstrate the existence of a Drude-free electron behavior, characteristic of a metal, have yielded negative results for the high pressure A phase. New techniques, such as NMR to understand the role of ortho-para concentration and electrical conductivity measurements to provide a rigorous test of metallization, are under development.

14. SUBJECT TERMS

propellant; hydrogen; metallic; pressure

15. NUMBER OF PAGES

35

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	SAR

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std 239-18
298-102

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.0 INTRODUCTION

Atomic hydrogen, because of its small mass and large recombination energy, is theoretically the most promising of all chemical propellants. Currently the best existing chemical propellant is the molecular hydrogen-oxygen fuel. Even in the liquid form, because of its low density, these fuels require large storage tanks, which add to the weight of a vehicle. Thus metallic hydrogen has two important advantages: it has a large specific impulse and its density will be more than an order of magnitude larger than that of ambient liquid hydrogen.

Together these factors provide enormous advantages in rocket propulsion and are the reason for investigating the feasibility of producing metallic hydrogen in the laboratory. It is now known that to produce the atomic metallic phase by the brute force method of compression of molecular hydrogen, pressures in the range of 2-5 megabars are required. Achieving pressures in the 1- to 2-megabar range, under careful laboratory conditions using diamond anvils, is now fairly routine. With some care, higher pressures have been achieved.

At high pressures metallic hydrogen is expected to exist in two forms: hydrogen first becomes metallic in the molecular phase, then transforms to atomic metallic hydrogen at higher pressures. The theoretical expectations for metallic hydrogen will be reviewed in the first section of this report, followed by experimental progress in producing metallic hydrogen. It is expected that hydrogen and its isotope deuterium will have very similar properties with regard to metallization, and some of the work to be discussed concentrated on deuterium.

Several years ago a new phase line was found to exist in hydrogen with a transition pressure of about 150 GPa in the zero-temperature limit. The nature of this new phase, named the hydrogen A-phase (H-A), has not yet been determined, but there is some evidence it may be the metallic molecular phase. The partial phase diagram of hydrogen and its isotopes in Figure 1 shows the pressure region of the A-phases and the triple point in deuterium.

Much of the research effort has been dedicated to understanding and extending this phase diagram and the interactions of hydrogen as a function of pressure. To understand the high pressure properties it is important to know how the system develops with pressure. Concentrating on hydrogen in the ground molecular rotational states (para-hydrogen or ortho-deuterium), it is noted that at low pressures these molecules are characterized by free rotor states with spherical harmonics as wavefunctions, the angular momentum, J, and its projection, m, as quantum numbers. Thus the ground state molecules have quantum numbers J=0, m=0 and are spherically symmetric; there is no orientational order of the lattice because of this.

At high enough densities the anisotropic interactions result in a change in the nature of the rotational states so that they are no longer spherical harmonic wavefunctions and the ground state is non-spherical. This happens as a phase transition to the broken symmetry phase (BSP). At this transition the molecules transform from a spherically symmetric phase to an orientational ordered phase. The phase line is shown in Figure 1 for hydrogen, deuterium (D), and hydrogen deuteride (HD). The phase lines for D_2 and HD have been studied in detail in this contract.

At still higher pressures of order 150 GPa (100 GPa=1 megabar) a transition to the A-phase is seen. Remarkably, this takes place at almost the same pressure for H_2 and D_2. It is the nature of this phase, which has been suspected of being the molecular metallic phase, where research has been concentrated. This research consisted of studying the lattice excitations and the order parameters and interpreting the behavior by using group theoretical treatments. From this work the phase lines for D_2 have been extended to include the A-phase and the triple point shown in Figure 1. A similar diagram is believed to exist for hydrogen, but in this case the less well-studied hydrogen was interpreted to have a critical point, not a triple point. It is now believed that hydrogen also has a triple point, which is a very important result that is discussed in Reference 1.
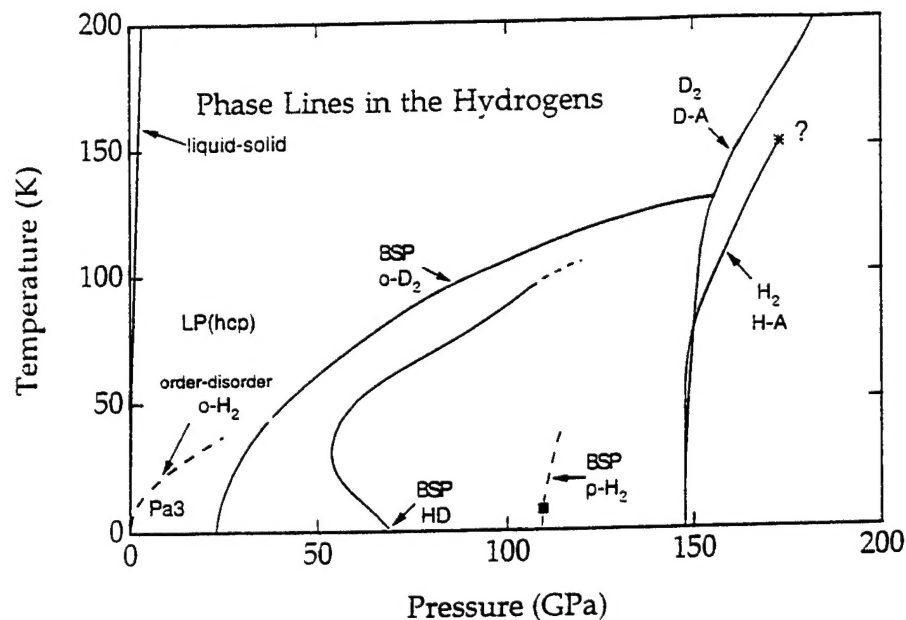
1

Figure 1
Partial Phase Diagram of the Hydrogens

To determine if the A-phase is metallic, the broad band infrared absorption was measured. If the lattice is metallic, then the electrons will have a plasma frequency. The sample strongly absorbs infrared radiation for frequencies lower than this. The low energy spectrum was extended to approximately 3300 cm^{-1} and it was found there was no strong evidence of metallization. The spectrum exhibited an interesting increase of absorption, but a decisive statement concerning the metallic state will require extension of the spectrum to lower frequencies. This work is in progress.

A second and more rigorous method of determining the metallic state is to measure the static electrical conductivity at the limit that the sample temperature goes to zero. This is a difficult task because electrical leads must be passed from the megabar to ambient pressure region of the apparatus. Extensive attempts to accomplish this have not succeeded and work is continuing.

To interpret the high density measurements it is important to know the equation of state in order to relate the pressure to the density and, therefore, the interatomic or intermolecular separations. Work is currently in progress on these measurements, as well as a determination of the index of refraction of hydrogen at megabar pressures.

With progress in the investigations of the hydrogens at very high pressure, it has become clear that the ortho-para nature of the solid samples may be very important for understanding metallization. However, ortho-para conversion has only been studied to 0.5 GPa. An NMR apparatus and techniques are being developed that will allow extending this technique to megabar pressures to determine the ortho-para content, as well as the proton-proton separation in the molecules as a function of pressure.

Finally, new methods to achieve high pressures are in the process of being developed. An apparatus for polishing diamonds has been built to polish culet shapes that could not be supplied by traditional diamond polishers. It is believed that this can help achieve higher pressures, which will also make the task of measuring DC conductivity easier.

The primary objective of this research is to produce metallic hydrogen in the laboratory and characterize this substance. Metallic hydrogen as a high pressure form was first proposed in 1935 and the effort to produce this in the laboratory has intensified since the 1950s. Progress toward producing metallic

2

hydrogen has been characterized by a joint theoretical and experimental effort. The first part of this report will discuss the current theoretical and experimental understanding of hydrogen, followed by a description of the contributions that have been made in the past three years under the support of the Air Force Phillips Laboratory Operating Location at Edwards AFB.

Hydrogen and its isotopes (deuterium, deuterium hydride, etc.), referred to collectively as the hydrogens, are prototype solids for classes of insulator-metal (IM) transitions. Mott (Ref. 2) introduced a model of hydrogen – electrons and protons – for the metal-insulator transition. He considered the transition from a low-density, insulating crystal of atoms with electrons localized around the protons to a high-density monatomic metal.

Nature has not allowed this behavior for hydrogen, because at low density a lower energy state is achieved by the electrons and protons pairing up to form molecules, which form an insulating crystal. At very high pressures this molecular lattice is expected to transform to an atomic metallic phase. Indeed, recognizing that at sufficiently high densities all insulators should become metallic, Wigner and Huntington (Ref. 3) had considered the problem of compressed molecular hydrogen and predicted that it would dissociate into an atomic lattice and become a metal. Kronig, de Boer, and Korringa (Ref. 4) later made the same prediction as they speculated that hydrogen might become metallic at the high pressures of the Earth's core where it might exist. Today it is not believed that the Earth's core contains metallic hydrogen, but De Marcus (Ref. 5) speculated about the possibility that the giant outer planet Jupiter, which is composed mainly of hydrogen and helium, might be metallic, even in the outer crust where megabar pressures exist.

The world still awaits the experimental observation of metallic hydrogen in the laboratory. The isotopes of hydrogen are isoelectronic and the mass variations are not expected to have a significant impact on the high-pressure properties. Thus the metallization of any of these isotopes will be a satisfactory demonstration of metallization in the hydrogens and any large variation in the metallization pressure of the different isotopes will be very surprising.

In 1968, Ashcroft (Ref. 6) predicted that atomic metallic hydrogen might be a BCS superconductor with a high, possibly room temperature, critical temperature. This exciting prospect stimulated continuing activity, both experimental and theoretical, to produce and understand this predicted new state of hydrogen. Brovman, Kagan, and Kholas (Ref. 7) showed that metallic hydrogen, much like the diamond-graphite system, might be metastable, meaning that once produced at high pressure, it would remain in a metastable phase when the pressure was released (i.e., the atoms do not fly apart when the pressure is released). However, Salpeter (Ref. 8) investigated another decay channel: hydrogen atoms at the surface might tunnel into the molecular form and evaporate away, so that the lifetime of this metastable phase might be very short.

Ramaker, Kumar, and Harris (Ref. 9) and, later, Friedli and Ashcroft (Ref. 10) showed that a different IM transition might intervene at intermediate pressures within the molecular phase of solid hydrogen. In this case, as the density is increased the electronic valence and conduction bands of the insulating molecular solid would overlap, leading to a metallic state. Thus the emerging picture that persists today is that as pressure is increased the solid molecular hydrogens first transform to the metallic state, remaining a molecular solid. At even higher densities the molecules dissociate, leading to the atomic metallic state proposed by Wigner and Huntington (Ref. 3). Brovman, et al. (Ref. 7) considered the effect of the zero-point motion of atomic hydrogen on the phase of metallic hydrogen. They found that even at these very high densities, in the atomic phase the zero-point energy was almost sufficient to render hydrogen a liquid at T=0 K.

This created interest in using metallic hydrogen as a high-energy density material. If metallic hydrogen could be produced and stabilized after release of the pressure, this material would be an important technological fuel, in particular for propulsion, because of the large energy release per mass of hydrogen when it is burned.

Spurred on by the many predictions for high density hydrogen, experimentalists accepted the challenge to study this material at pressures predicted to require access into the multimegabar region. Early

experiments focused on generating high pressures for short periods of time through the use of shock or explosive techniques. More recently, with the advent of the diamond anvil cell (DAC), static pressures in the 2-3 megabar pressure range have been achieved on hydrogen; even higher pressures should be accessible.

2.0 THEORETICAL PROSPECTS FOR METALLIC HYDROGEN

Early calculations of the IM transition were difficult in that the molecular and atomic phases were controlled by different theoretical methods and much more uncertainty existed in the free energy of the more complex molecular phase (Ref. 3). The large uncertainty in the free energy of the molecular phase resulted in a large scatter of the predicted critical pressure of the IM transition because the many calculations in the literature used different forms of the free energy. Moreover, calculational techniques did not correctly predict the pressure for band gap closure in the molecular case.

Although current approaches do not suffer these problems, the density functional approach used most commonly has not been able to incorporate the important zero-point energy in the formalism. That, combined with its inability to properly account for the rotational states of the molecules, creates an array of results, all with uncertainty as to both the ground state structure and the critical pressure for the transition to the metallic state. In principle, the Green's function Monte Carlo technique should be able to resolve these problems, but it is difficult to apply and there have only been a few serious, but limited, studies using this method (Refs. 11, 12).

In the current theoretical approach for predicting the IM transition, a series of structures are chosen and the total energy and band structures are calculated. The lowest energy structure as a function of density is then selected as the stable state and the critical density is determined. One of the serious caveats for this approach is that the true structure may not be among the group of structures considered.

The first predictions for the formation of atomic metallic hydrogen were limited by both the calculational techniques available in the early days of quantum mechanics and a lack of knowledge of the equation of state (EOS) of hydrogen. The EOS is important because theoretical calculations of the transition consider the free energy as a function of the crystal density to determine a critical density for metallization. The critical density is related to the critical pressure, the experimentally available tool for varying the density, via the EOS. Most modern calculations are still not capable of accurately predicting the EOS because of difficulties with incorporating the zero-point energy. These calculations usually rely on the extrapolated experimental EOS, which is considered to be fairly reliable, and will be discussed later. This creates an inconsistency in these predictions. The calculation of Wigner and Huntington (Ref. 3) predicted a critical pressure of about 0.25 megabar, which is incorrect because experiments have exceeded 2 megabars without detecting this state. Modern calculations indicate that this transition will take place in the 3-5 megabar range.

This report first addresses the band overlap metallization in the molecular phase. Although there have been a large number of calculations of the metallization pressure of hydrogen, attention will be given to those that are currently most important or those with the largest impact on the field.

2.1. Metallic Molecular Phase

The first theory of molecular metallization by Ramaker, Kumar and Harris (Ref. 9), as well as by Friedli and Ashcroft (Ref. 10), calculated the electronic band structure of hydrogen and found the density for band overlap metallization. Overlap was found to be indirect, between the valence band and a zone-edge conduction band, so that the number of charge carriers would be small and the metal would be considered a semi-metal. The high pressure EOS was only crudely known at the time, but this was not the greatest limitation. The only structure that was used in both calculations was the Pa3 crystal structure, which has the molecular axes oriented along the body-diagonals of a face centered cubic (fcc) lattice, as shown in

Figure 2. A critical pressure of about 1 megabar was predicted. The Pa3 structure had already been experimentally determined to be the ground-state structure of solid ortho-hydrogen (ortho-para considerations will be discussed later) at ambient pressures. This orientationally ordered structure minimizes the lattice energy for electric quadrupole-quadrupole (EQQ) interactions between molecules when the Hamiltonian for anisotropic interactions is restricted to a sum of pair interactions.
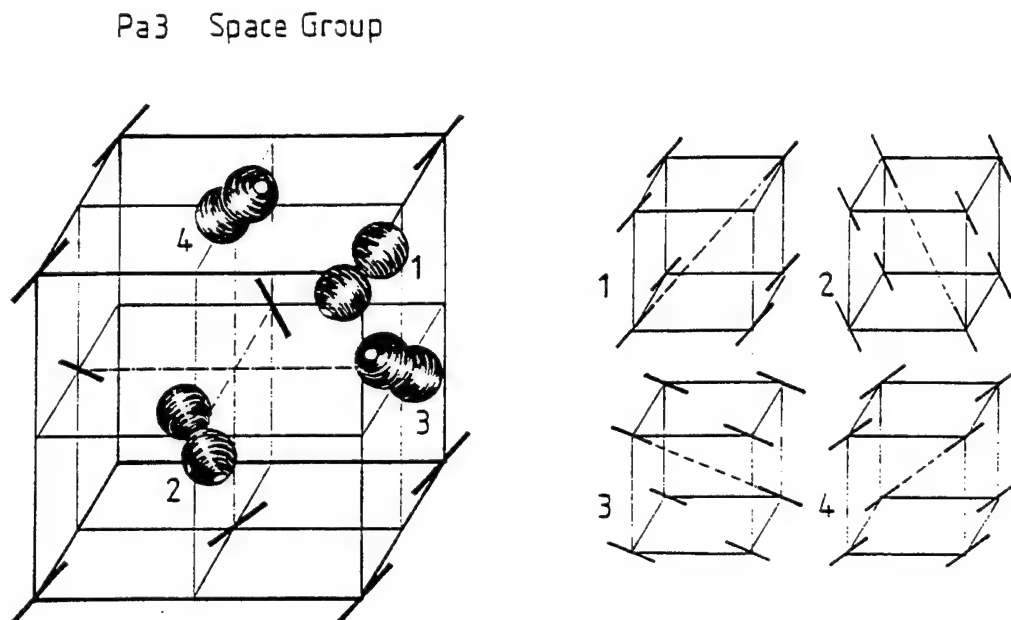
Pa3   Space Group

Figure 2
Pa3 Crystal Structure

In the 1970s it was found that accurate predictions of properties of atomic solids could be obtained by using the density functional method in the local density approximation (LDA) for calculating the ground-state total energy of a crystal (Ref. 13); this method implicitly incorporates the many-body electronic forces. In 1989 Barbee, Garcia, Cohen, and Martins (Ref. 14) applied the LDA method to molecular hydrogen by using a r^{-1} potential between charged particles, rather than a pseudo-potential, and an appropriate form of the exchange and correlation energies; zero-point energy based on a harmonic approximation was added to the total energy at each density. Quantum mechanical rotational states were not used for the orientational distributions of the molecules, but a so-called ball-and-stick model was employed. In this model the protons are separated by the bond length and the nuclei are clamped so that the molecular axes are rigidly aligned in the solid.

This general approach has been followed in subsequent calculations by others. The work of Barbee, et al was motivated by the observation of a phase transition in hydrogen at 77 K and 150 GPa, which had been interpreted as a transition to orientational ordering. This is now known as the hydrogen-A phase and will be discussed in detail later. They wanted to investigate the possibility that the A-phase was of a different origin, perhaps the IM transition. They calculated the total energy for a number of structures as a function of density. They then plotted the change in energy (or free energy, DH or DG) versus the density; the structure with the lowest free energy at a given density is the most stable structure of the group that has been studied. Structures considered were: the simple cubic (sc), face-centered cubic (fcc), body-centered cubic (bcc), Pa3, primitive hexagonal (ph), and hexagonal close-packed (hcp), or hcp-c, a lattice

with molecules oriented along the c-axis, and having the same symmetry as hcp. At low pressure they found Pa3 was the lowest energy structure, going over to hcp-c at a pressure of about 50 GPa (100 GPa=1 megabar). The ph lattice became the stable structure above a pressure of 380 GPa. These results are shown in Figure 3a. The LDA accurately determines the ground state energy; however, the electronic band structure, which is also derived, has band gaps that are too small. Thus if band gap closure metallization is predicted in the LDA it will give too low a value for the critical pressure. For hcp-c, the band gap closes, at submegabar pressures, far lower than expected. The earlier prediction that Pa3 would become metallic was inadequate for two reasons: predicted band gap splittings were not accurate and Pa3 is not the lowest energy lattice. Together, these two effects resulted in the prediction of a critical pressure in the megabar region, which is now believed to be the region of interest.

The next development was that Garcia, Barbee, Cohen, and Silvera (Ref. 15) conducted a more detailed study of the hcp structure, focusing on the possibility of band gap closure metallization. Ashcroft (Ref. 16) had recently shown that orientational order might have a substantial effect on the metallization pressure of hydrogen. Garcia, et al studied the hcp-c ball-and-stick model and hcp-s (a model in which the electronic distribution is spherical at the molecular sites to simulate orientationally disordered hydrogen). They found a substantially larger gap for the hcp-s hydrogen than for oriented hydrogen. For hcp-c using the LDA, they found band gap closure at 95 GPa. Since the LDA does not correctly predict band gaps, a commonly used procedure called the scissors-operation was used to correct the calculation and predict metallization at 270 GPa. The band energies calculated as a function of density are linearly translated in energy to give a band gap that agrees with the experimentally known value. The translation increased the gap by about a factor of 2.
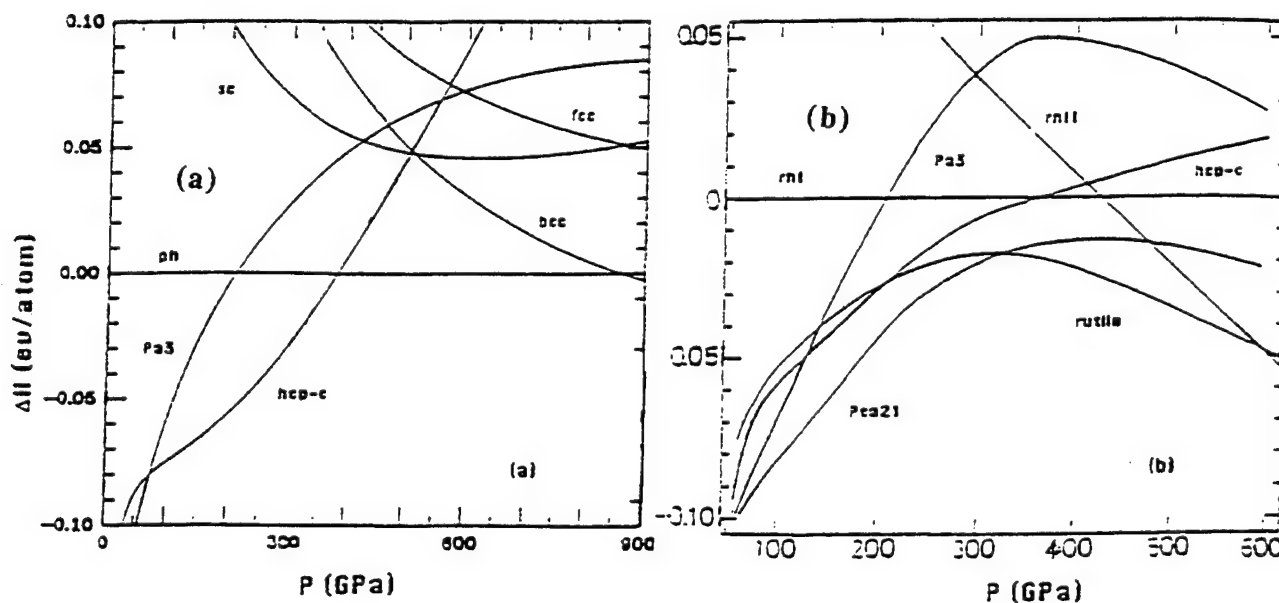
Figure 3
Free Energies of Molecular Structures

To improve on this ad-hoc technique, Garcia, et al modified the LDA with the Slater X-α scheme, determining the parameters by forcing them to agree with low pressure experimental results. This predicted metallization at 180 ± 20 GPa for hcp-c was in reasonable agreement with the A-phase transition pressure. Chacham and Louie (Ref. 17) then did an improved calculation and found a metallization pressure of

150 GPa for hcp-c hydrogen. This supported the theory that the A-phase was metallic in the hcp-c structure.

Kaxiras, Broughton, and Hemley (Ref. 18) conducted an LDA calculation to further examine structures in which the molecular centers are on an hcp lattice but are oriented away from the crystal c-axis. They found lower energy structures than hcp-c, with larger gaps that would imply higher metallization pressures. Kaxiras and Broughton (Ref. 19) took that a step farther and found lower energies for structures on the hcp lattice, still considering only two molecules/unit cell. Although their lowest predicted energy is for the Pmc2$_1$ structure, the P2/m structure shown in Figure 4 seems to be the most consistent with infrared studies of the vibron modes that were conducted (Ref. 20). These results cast serious questions concerning the nature of the hydrogen A-phase because the lower energy structures have larger band gaps and, thus, higher critical pressures. Similar to the study of Barbee, et al, Nagara and Nakamura (Ref. 21) studied the hcp lattice, enlarging the unit cell to 4 molecules and found still a lower energy structure with space group Pca2$_1$; above 300 GPa the structure was predicted to become rutile as shown in Figure 3b, which can be compared to the results shown in Figure 3a. Some of these structures are shown in Figure 4. The theoretical situation became further confused when Surh, Barbee and Mailhiot (Ref. 22) considered the effects of zero-point energy and found that this would again lower the energy of hcp-c below that of Pca2$_1$. Recently, Edwards and Ashcroft (Ref. 23) proposed that the layered structure, space group Cmca with 4 molecules/unit cell, might have yet a lower energy.

P2/m

Pca2$_1$

hcp
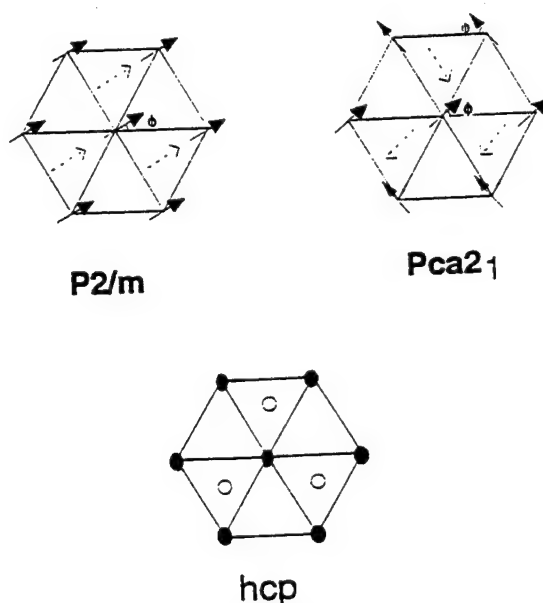
Figure 4
Structures of H$_2$ at High Pressure

Thus the theoretical picture of the molecular metallic state is currently unclear. Anticipating some experimental results to be discussed later, it has been shown that the hcp-c and Cmca are inconsistent with infrared absorption data in the A-phase. It should be noted that none of the above theories have correctly incorporated the molecular orientational distributions, which might have an important effect on the metallization pressure. It could also be that crystals of mixed ortho-para concentration, which have for the most part been studied experimentally, might lead to Anderson localization: the orientational state randomly changes from site to site so that electrons encounter random potentials and are localized. An even more profound question is: even if the lattice is a pure species, and since the electronic motions are much faster

than the nuclear motions, will the electrons moving through the lattice encounter randomly oriented pairs of protons, rather than the distributions described by the nuclear part of the molecular wavefunctions? Some of these aspects have been addressed by Ashcroft (Ref. 24).

2.2 Atomic Metallic Phase

The most important questions asked of the theory for atomic metallic hydrogen are the following: What is the critical pressure for the transition from the molecular to the atomic phase? What will be the critical temperature for superconductivity? What will be the spatial structure? Will it be metastable at zero pressure? The current state of affairs is that none of these questions have a precise answer. Estimates of the critical pressure for the transition, P_c, have varied from 0.25 to 20 megabars, although it is now believed that it will be in the 3-5 megabar range.

Many calculations of the critical pressure had uncertainties in the predicted critical pressure for the transition because of the use of a Hamiltonian for the molecular phase based on sum-of-pair interactions. At high pressures many-body interactions become important and the sum-of-pairs approximation is inadequate. At zero pressure the intermolecular separation is 3.79Å, while the proton-proton separation within a molecule is 0.74 Å. There is essentially no electronic overlap between nearest neighbor molecules where intermolecular interactions can accurately be described by a multipolar expansion of the Coulomb charge. The most important term in this expansion is the isotropic interaction potential. Since three-body terms are very weak, interactions are accurately described by a pair Hamiltonian for isotropic and anisotropic interactions, the latter being dominated by the EQQ interaction. As the pressure is increased the density grows rapidly, with an approximately 10-fold increase at 1 megabar, while the proton-proton separation only changes modestly. In this pressure range electronic overlap becomes important and a many-body approach to interaction energies must be used to get meaningful results. The LDA approach seems to do a good job of incorporating the many-body forces; however it does not embody the zero-point motion.

In a paper, Brovman, Kagan, and Kholas (Ref. 7) considered the metastable structures of metallic hydrogen at zero pressure. They used a perturbation approach for calculating the Coulomb energy and found the stable structures that were allowed, after adding in the zero-point energy arising from the lattice motions. The metallic phase was stabilized over the molecular phase by a barrier of order 1 eV/electron. They found an unusual filamentary structure with two-dimensional periodicity. Protons were very strongly bound along the filament so that a triangular lattice of filaments formed, in which the chains were weakly bound to each other. They then calculated the properties of metallic hydrogen under pressure (Ref. 25), finding that the highly anisotropic structures become more and more symmetric with increasing pressure. At about 0.25 megabar the filamentary structure goes over into a family of planar structures; at still higher pressures the fcc lattice is stabilized and then the bcc and hcp structures are stabilized. They did not estimate P_c because of the uncertainty in the energy of the molecular phase, noting that the variance in quoted values of this quantity in the literature was quite large.

Brovman, et al also noted the possibility that metallic hydrogen might be a liquid because of the large zero-point energy. According to their calculations, the high pressure phase might only be crystalline at T=0K and loses long-range order for finite temperatures. They noted that the liquid phase might even be more stable than the crystalline phase and would require detailed calculations of the thermodynamic potential of the liquid state as a function of pressure to determine the equilibrium phase. Thus with increasing pressure the atomic metallic lattice might melt, crystallize and, ultimately, melt again at extremely high pressures when the zero-point energy becomes dominant.

The most complete study of the question of the existence of a liquid state at high pressure and T=0K is by Mon, Chester, and Ashcroft (Ref. 26), who used variational and Monte Carlo techniques to compare the liquid and solid energies at low pressures compared to the extremely high pressure at which the zero-point energy leads to quantum melting. Although for most densities they found the solid to have a lower energy than the liquid, for a value of $r_s=1.6$ ($r_s=[(3/4\pi) (a_o^3/\rho)]^{1/3}$), where ρ is the electron or nucleon

density and a_o the Bohr radius) the energies were equal to within the precision of the theory. This result was found for both hydrogen and deuterium for a pressure just under 1 megabar. If molecular hydrogen is converted to a metal at several megabars, the liquid state might be reached by reducing the pressure somewhat below the critical pressure so that the atomic hydrogen is in the metastable region. If atomic metallic hydrogen was a liquid, this would mean a fermi surface exists for both the electrons and protons. For deuterium one would have the possibility of superconductivity in the electronic fluid and superfluidity of the deuterons that are charged boson particles. Oliva and Ashcroft have considered some of the thermodynamic properties of liquid metallic hydrogen (Ref. 27) and deuterium (Ref. 28).

Perhaps the most highly regarded calculation of the critical pressure for the IM transition to the atomic state is by Ceperley and Alder (Ref. 11). They performed quantum Monte Carlo (QMC) calculations of the properties of molecular and atomic hydrogen for a number of densities at zero temperature. In these calculations the interactions are between electrons and protons on selected lattices and the zero-point energy is intrinsically included in the formalism. For the molecular phase they used four lattices: isotropic fcc, ordered fcc (Pa3 structure), bccp (cubic with molecules aligned along the [111] direction), and the γ-nitrogen structure (ordered on a bcc lattice). Of these, they found Pa3 to be preferred at high pressure; reasonable agreement was found between the theoretical and experimental EOSs in regions of overlap. Between 1 and 2 megabars they found evidence of a possible transition from isotropic fcc to the orientationally ordered Pa3 lattice. They did not investigate the possibility of metallization in the molecular phase. Their considerations were for densities corresponding to megabar pressures; they did not find evidence of the planar structures found by Brovman, et al and confined their studies to the sc, bcc, and fcc lattices. The sc had a larger energy than the bcc and fcc, whose energy differences were smaller than the error bars. They found that hydrogen changes from an fcc molecular phase to a cubic atomic phase at a pressure of 3 megabars, with a relative volume change of 20% at the transition. Later, Natoli, Martin, and Ceperley (Ref. 29) performed a QMC calculation, further considering the structure of the metallic state by extending the lattices to lower coordination structures. They found the diamond structure to be energetically favored in the 3-megabar region.

The main criticism of these studies is that they were too limited in the selection of lattice structures. For example, based on LDA calculations it is now believed that at high pressures the lattice for the molecular centers is hcp, not Pa3. Recent experimental results seem to exclude the Pa3 structure (Ref. 30). A molecular lattice with an energy lower than that of the Pa3 lattice would increase the calculated value of P_c for the transition to the bcc or fcc atomic phase (Ref. 12).

2.3 Stability of the Zero-Pressure Atomic Metal

In the consideration of the predicted metastability of atomic metallic hydrogen, Salpeter (Ref. 8) proposed that even though metastability might exist in the interior of a crystal, at the surface neighboring atoms could tunnel from the atomic into the molecular state and then evaporate away. Although this is estimated to occur very slowly, the removal of a pair of atoms from the surface leaves a hole, and atoms in the vicinity of such impurities can tunnel at a substantially higher rate. Estimates of the tunnel barrier were quite crude and the uncertainty in the results were very large. The typical lifetime of a macroscopic crystal was estimated to be between less than 1 msec to 100 seconds. The uncertainties are large enough that one really must appeal to future experiment or improved theory. The virtue of this calculation is that it provides a mechanism for decay of zero-pressure atomic hydrogen. A modest pressure should greatly increase the lifetime, and it is possible that a sample in a diamond cell pressed against surfaces of diamond and the confining gasket might have enhanced lifetimes over free-standing crystals. Calculations of the molecular metallic state do not indicate metastability of this phase at pressures reduced below the critical pressure.

2.4 Superconductivity of Atomic Metallic Hydrogen

Ashcroft (Ref. 6) first predicted that atomic metallic hydrogen might be a high T_c (critical temperature) superconductor. His considerations were based on a BCS model, without consideration of crystal structure or calculation of the electron-phonon interaction. Barbee, Garcia, and Cohen (Ref. 31) carried out a detailed calculation on a proposed lattice, a distorted primitive hexagonal lattice considered at 4 megabars. They used a frozen-phonon method to calculate the lattice dynamics and the electron-phonon interaction. For the strong-coupling theory they found the critical temperature to lie between 145 and 300 K. This general theoretical approach yielded accurate results when applied to silicon and compared to experiment. Again, in this case the caveat is that metallic hydrogen may not have the structure that they considered, but their results show that metallic hydrogen could easily turn out to be a room-temperature superconductor. Although they did not conduct detailed calculations, they suggested that the molecular metallic phase might also exhibit high T_c superconductivity.

3.0 PROPERTIES OF THE MOLECULAR PHASE

The only experimentally established phase of the solid hydrogens is the molecular insulating state. To recognize a transition to the metallic phase, the properties of the low pressure hydrogens should be understood (Ref. 32). A number of aspects of importance will be considered here: the ortho-para distinction, the EOS, and phase transitions to states of orientational order.

3.1 Ortho and Para Species

The identical particle nature of the nucleons in hydrogen imposes quantum mechanical restrictions on the wave functions of the molecules. For isolated hydrogen molecules, because of the spin 1/2 of the protons, the wavefunction must be antisymmetric under permutation of the nucleons. Consider restriction on the product of the rotational and nuclear spin wave functions. The nuclear spin state has the total spin $I = i_1 + i_2 = 0$ or 1, which are antisymmetric and symmetric states, respectively. The rotational wave functions are spherical harmonics with angular momentum quantum numbers J and M; these wavefunctions are symmetric for even J and antisymmetric for odd J under permutation. Thus the nuclear spin zero states couple with the even-J; this is called para-hydrogen (p-H_2). The spin-1 state couples with odd-J; molecules in these states are called ortho-hydrogen (o-H_2). The nomenclature changes for deuterium, which has a spin-1 nucleon and the wavefunction is symmetric under permutations. Ortho-deuterium (o-D_2) corresponds to the (I; J)=(0,2; even) wavefunctions and para-deuterium (p-D_2) to (1; odd) wavefunctions. These considerations do not apply to mixed isotopes such as HD since the nucleons are not identical particles.

The most important aspect of the ortho-para considerations is that molecules of a given species are metastable; conversion from ortho to para is strongly forbidden for isolated molecules. In the solid at low pressure the single molecule wavefunctions described above are only slightly distorted; the ortho-para distinction remains valid. Conversion takes place very slowly because of magnetic field gradients from neighboring molecules in both hydrogen and deuterium and electric field gradients in deuterium (which has a spin-1 and thus has a nuclear electric quadrupole (EQ) moment. For hydrogen the rate of conversion is quadratic in the concentration of the species, and pure (100%) ortho-hydrogen converts at about 1.9%/hour in the zero-pressure solid (Ref. 32). For deuterium the rate has a linear term (because of the EQ moment) as well as a quadratic one and, because of the much smaller nuclear magnetic moment, the rate for 100% para-deuterium is 0.06%/hour at zero pressure. At zero pressure a pure o-H_2 sample will require about a week to approach the equilibrium concentration at 4.2 K (essentially 100% para). At 77 K the equilibrium concentration is approximately 50-50 ortho-para for hydrogen.

At very low pressure (0-1 GPa) the conversion rate first increases and then decreases (Ref. 33). It has been observed that at elevated pressures on the order of 20 GPa or higher, the conversion rate becomes

much faster and samples convert to equilibrium within about 24 hours. There have been no detailed studies of the ortho-para concentrations or conversion rates at high pressure. These results are based on observation of temporal changes of rotational spectra. Furthermore, the equilibrium concentrations of ortho-para are not known at elevated pressures. This equilibrium depends on the rotational energy level spectrum, which undoubtedly changes at higher pressures.

3.2. The Equation of State

The equation of state of hydrogen and deuterium is known experimentally to be about 40 GPa. A substantial amount of work was conducted at low pressures to 2 GPa and will not be discussed here because it was reviewed in the work by Driessen and Silvera (Ref. 34). A large improvement in knowledge of the high pressure EOS came from diamond anvil cell work on hydrogen and deuterium to pressures of 37 GPa. Van Straaten and Silvera (Ref. 35) measured the volume and pressure of samples at 5 Kelvin. They fit their data to a form that should have the proper physics at high pressure so that their curves could be extrapolated. The main problem with this determination was that the volume measurement had a large uncertainty, up to 5%. Shimizu, Brody, Mao, and Bell (Ref. 36) studied hydrogen by Brillouin scattering to 20 GPa, from which an EOS was extracted. Comparison of these two experiments differed by more than the experimental error bars. In principle the Brillouin measurement can give high precision results; evidently these measurements suffered from possible contamination of the hydrogen (Ref. 37) as well as interpretational problems from not taking into account elastic anisotropy. Recently, Zha, et al (Ref. 38) studied single crystals of hydrogen by Brillouin scattering at pressures up to 24 GPa and found excellent agreement with the EOS, determined by X-ray techniques.

The most accurate and direct method for determining the EOS is to measure the lattice constant by X-ray or neutron diffraction. X-ray studies were conducted by Hemley et al (Ref. 39) on crystals grown in a DAC for both hydrogen to a pressure of 26.5 GPa and deuterium to 14.2 GPa. Although the highest pressures are lower than the direct measurement of volume approach, the precision is much greater. Nevertheless, for the hydrogen, measurement agreement in the region of overlap was to within 0.1%. For deuterium, the measurements were within experimental error, but differences were as much as 5%. Hemley, et al also fit their data to an analytic function that could be extrapolated. Both this and the extrapolated EOS of van Straaten and Silvera give very similar results in the 1-2 megabar region, and they seem to be accepted as the best results. Neutron diffraction measurements have been performed by Ishmaev, et al (Ref. 40) at modest pressures and Glazkov, et al (Ref. 41) on deuterium to 30.9 GPa, filling in important points of the EOS. All of the diffraction measurements are consistent with an hcp structure for hydrogen and deuterium at room temperature.

It would be very useful if the EOS could be measured in the megabar region. It is difficult to extend the single crystal growing techniques into the 100 GPa range so that the direct volume method has the most promise of future extensions. A program using a method developed earlier (Ref. 35) has been started. The volume of the sample in the gasket is measured. The sample area, A, is measured photographically, using a video frame grabber to capture an image that can be processed with a computer. The thickness is measured from the interference fringes arising from the Fabry-Perot interferometer formed by the two diamond culets containing the hydrogen. In this case 2nd is measured, where n is the index of refraction of the hydrogen and d is the thickness of the sample. The product Ad gives the sample volume and the pressure is determined by ruby fluorescence. The main problem has been to separate the product nd. A method has now been developed to independently measure n by measuring the reflection from the sample. The index itself is an important physical quantity for understanding metallization of hydrogen. At the present time the sample pressure is about 65 GPa, and results for the index measurement are shown in Figure 5.
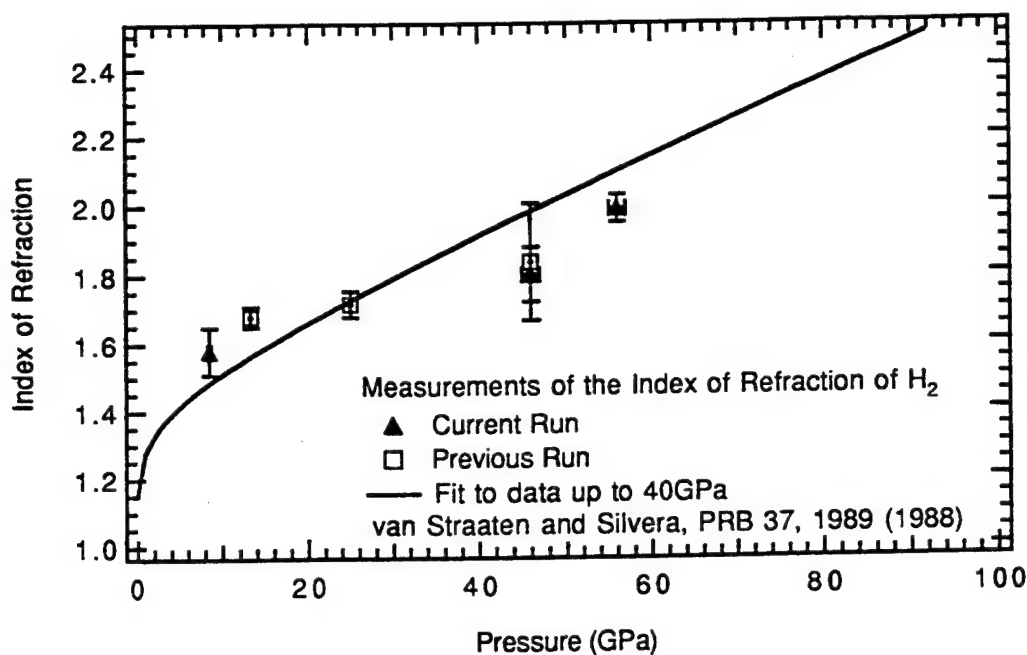
Figure 5
Index of Refraction of Hydrogen as a Function of Pressure

3.3 Orientational Order Phase Transitions

The earliest interest in solid hydrogen was the phase transition to an orientationally ordered structure that takes place at low temperature and pressure. High purity o-H_2 (p-D_2) solidifies at just under 14 K into an hcp lattice. At low temperature only the J=1 rotational level is populated and the molecular axes orient randomly in space so that the lattice is orientationally disordered. At T=2.8 K (3.8 K) the lattice orientationally orders into the Pa3 structure shown in Figure 2. This structure minimizes the energy for the EQQ interaction, which is the dominant anisotropic interaction. Silvera and Jochemsen (Ref. 42) studied the critical temperature as a function of pressure to about 0.5 GPa and found that it increased as expected for an EQQ interaction with a R^{-5} dependence on intermolecular separation.

By contrast, pure p-H_2 solidifies at 13.9 K in the hcp lattice and remains in this structure to zero Kelvin. The molecules are in the single molecule J=0 rotational states, which are spherically symmetric and thus cannot orientationally order. Raich and Etters (Ref. 43) first predicted that at a sufficiently high pressure when the anisotropic interactions are sufficiently strong, J would no longer be a good quantum number. This manifests itself as a quantum transition at zero temperature. At the critical pressure the ground state wave function distorts from the spherically symmetric J=0 state to a state with lower symmetry. The molecules then orientationally order. This phase was called the Broken Symmetry Phase (BSP) by Lagendijk and Silvera (Ref. 44); the phase lines are shown in Figure 1.

This transition was first observed to have a critical pressure for the onset of the transition at T=0 K in o-D_2 at 28 GPa by Silvera and Wijngaarden (Ref. 45); subsequently it was observed in p-H_2 at 110 GPa by Lorenzana, Silvera, and Goettel (Ref. 46). The measurement of the BSP phase line in HD was performed in the current contract by Moshary, Chen, and Silvera (Ref. 47), who found the critical pressure to be 69 GPa. This was measured by studying the discontinuity in the Raman active vibron of HD. For hydrogen and deuterium it is expected that the transition temperature will increase with pressure. However, in HD the phase line has a very unusual shape because of the lack of metastability of even and odd rotational states.

12

To understand this, note that the critical pressure is very sensitive to even a small concentration of the J=1 species, because this species has a non-zero expectation value for the electric quadrupole moment whose fields induce moments in neighboring molecules. In hydrogen and deuterium, the J=1 species cannot be thermally populated, whereas in HD they can. Thus as the temperature is increased, the J=1 species is populated and the critical pressure for T>0 shifts down. Eventually, when the temperature is sufficiently high the system will thermally disorder. Then, an increase in the pressure causes an increase in the strength of the anisotropic interactions and, thus, the critical temperature and pressure. This results in the unusual boomerang-shaped phase line for HD. The crystal structure of the BSP phase is unknown.

The earlier work on the BSP phase line by Silvera and Wijngaarden was limited in pressure from 28 to 37 GPa. In this contract period, using the infrared (IR) absorption lines, the BSP phase line has been followed to much higher pressures and temperatures, with the result that it ends at a triple point between the A phase and the low pressure phase, as shown in Figure 6. For mixed ortho-para crystals of hydrogen or deuterium, the phase line lies between that for EQQ ordering and the BSP.
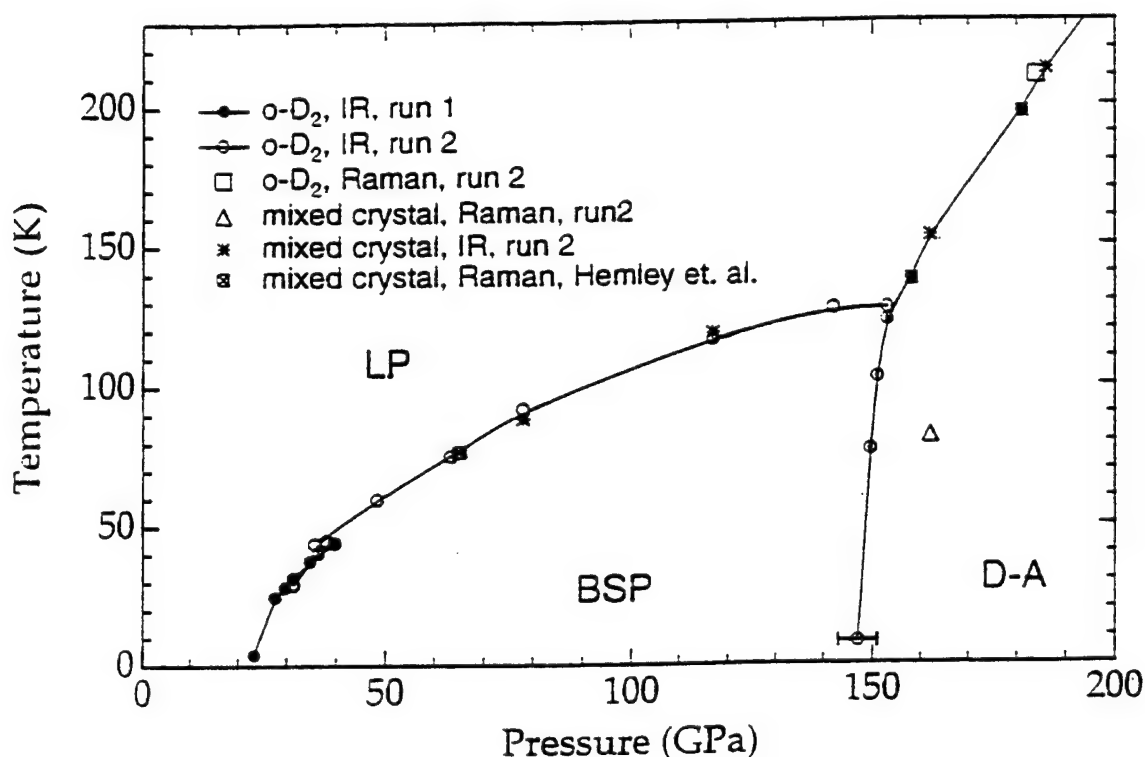

Figure 6
Phase Diagram of Solid Ortho-Deuterium

4.0. EXPERIMENTAL ATTEMPTS TO METALLIZE HYDROGEN

One of the great challenges to condensed matter physics has been to produce metallic hydrogen in the laboratory. A successful demonstration of any production of metallic hydrogen must pass stringent tests. The most rigorous method of demonstrating that a material is metallic is to show that its direct current (DC) electrical conductivity remains finite in the limit that $T \rightarrow 0$ K. This proof eliminates non-metallic conductors such as semiconductors or materials with Anderson localization. It is, however, very difficult to measure static conductivity in a megabar pressure vessel. A second method is to measure the electromagnetic reflection or absorption by the sample. An insulator will typically have a low reflectivity

and absorption, except in certain spectral ranges. On the other hand, a metal can be reasonably well described by the simple Drude free electron model. The isotropic Drude model with equal electron and hole masses m yields expressions for the real and imaginary parts of the dielectric constant, $\varepsilon \equiv \varepsilon_1 + i\varepsilon_2$:

$$\varepsilon_1 = n^2 - k^2 = \varepsilon_{IB} - \omega_p^2 \tau^2/(1+\omega^2\tau^2), \quad \varepsilon_2 = 2nk = \omega_p^2 \tau/\omega(1+\omega^2\tau^2)$$

Here, $N \equiv n+ik$ is the complex refractive index, ε_{IB} is the dielectric contribution from interband transitions, $\omega_p = (4\pi\rho e^2/m)^{1/2}$ is the plasma frequency for electron density ρ, and τ is the electron relaxation time. The absorption coefficient is given by $\alpha = (2\omega/c)k$. The absorption (in terms of optical density, OD) for sample thickness d is given by Beer's law, $A = \log(I_0/I) = 0.434\alpha d$, and the reflectance for normal incidence is given by the Fresnel equation, $R = |n+ik-n_D|^2/|n+ik+n_D|^2$, where n_D is the refractive index of the medium that interfaces to the sample, such as diamond in a DAC. For infinite relaxation time (no electron scattering), the sample reflection is unified below the plasma frequency and determined by ε_{IB} above; the radiation does not penetrate the sample below ω_p so there is no absorption. For finite τ the sharp edge of the reflection is broadened and the absorption rises steeply below ω_p. In highly compressed samples one may expect a high density of defects and a large scattering rate. In this case, detailed evaluation shows that the absorption and reflection may rise very slowly in the vicinity of the plasma frequency. As seen from the equations above, the details of the absorption and reflection will depend on both n and n_D.

The earliest attempts to metallize hydrogen used either very large presses to generate static pressures or shock techniques to generate transient high pressures; currently the most promising method is to generate static pressures in a diamond anvil cell. A giant press was built in the Soviet Union, but no results on hydrogen were ever published. There have been a number of claims of metallization of hydrogen. Grigor'ev, et al (Ref. 48) shock compressed hydrogen to high density and measured the EOS. They identified an anomaly in the pressure-density curve calculated to be at 2.8 megabar as the transition to the metallic state. No conductivity measurements were made. This claim was later retracted. Kawai, Togaya, and Mishima (Ref. 49) compressed preloaded hydrogen in a split-sphere, eight-cube assembly until conductivity was observed between electrodes across the sample. However, the data was limited and there was no satisfactory demonstration that the observation was not caused by short circuiting of the electrodes.

Vereschagin, Yakovlev, and Timofeev (Ref. 50) used a diamond indentor made of conducting carbonado diamond to measure the conduction across the sample and reported a transition to a metallic state. However, the highly compressible sample was ungasketed. It is suspected that the hydrogen was pushed out from under the tip so that, at most, a monomolecular layer of hydrogen existed. Again, this report could be caused by shorting or tunneling through the layer.

Hawke, et al (Ref. 51) used explosive magnetic flux compression to compress hydrogen to high densities and very high temperatures and used a microwave reflection technique to measure the conductivity. They reported a conductive state at a pressure calculated to be 2 megabars. In 1989 Mao and Hemley (Ref. 52) reported evidence of metallization of hydrogen in a diamond anvil cell with a gradual transition at static pressures in excess of 200 GPa. Their sample was in a gasketed diamond cell in the interstices of powdered ruby. Their evidence consisted of darkening of the hydrogen and optical absorption and reflection spectra on the micron-sized regions of hydrogen. Silvera (Ref. 53) criticized this claim on several issues. Blackening of a sample is not evidence of metallization and this sample was black, not only in the high pressure regions of the anvil, but also in substantially lower pressure regions at the edge. The optical measurements were in a limited spectral range and, although the reflectivity had the correct behavior, the evidence presented for the absorption spectrum actually was characteristic of an insulator, not a metal.

Still one more claim exists for the metallization of hydrogen, that the A-phase may be the molecular metallic phase. It is currently a controversial subject and will be discussed in detail below. The A-phase is a recently observed new phase in hydrogen and deuterium that exists for pressures higher than

about 150 GPa. It has been suspected of being the metallic molecular phase, but at this time there is no evidence to support this proposition.

In 1988 Hemley and Mao (Ref. 54) reported the observation of a phase transition in hydrogen at 150 GPa and 77K in a DAC. They found a discontinuity in the frequency of the vibron mode observed by Raman scattering, with a downward shift in frequency of approximately 100 cm^{-1} as the pressure was increased. They interpreted this as a transition to orientational order, an extension of the well-known disorder-order transition to the Pa3 structure caused by EQQ interactions, studied at much lower pressures (Ref. 42). Lorenzana, Silvera, and Goettel (Ref. 55) then studied a sample of hydrogen in this pressure range. Their objective was to trace out the P-T phase line. Rather than finding the point of Mao and Hemley on a curve extending back to the low pressure EQQ ordering line, they found a phase line that only existed at high pressure, with an onset at about 149 GPa in the T=0 K limit, rising sharply with increasing pressure, as shown in Figure 7. The phase line was independent of ortho-para concentration to within experimental error. This apparently was a new high pressure phase of hydrogen they named the hydrogen-A or H-A phase. Hemley and Mao (Ref. 56) then observed a similar transition in D$_2$ at 77 K and 190 GPa. This value of the critical pressure was subsequently reduced to 165 GPa because the first sample evidently suffered from large pressure distributions. More recently, Cui, Chen, Jeon and Silvera (Ref. 57) reported the transition pressure in deuterium to be 150 GPa, as observed by IR vibron absorption. The A-phase is molecular as the vibron excitation, characteristic of a molecule, persists in this phase.

It was suspected that the H-A phase was the metallic molecular phase. One reason was that the large negative shift of frequency at the discontinuity might correspond to transfer of electronic charge density from the molecular bond into a metallic bond. This would weaken the bond and lower the vibron frequency.
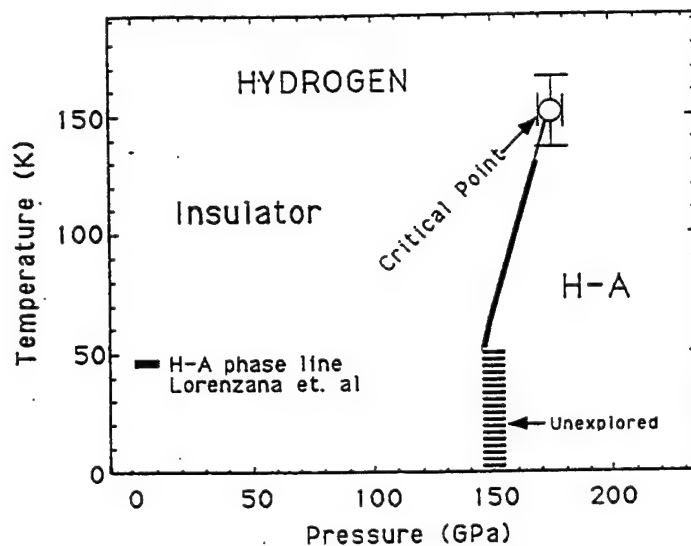

Figure 7
Phase Diagram of Hydrogen

Furthermore, electronic band structure theories seemed to support this idea (Refs. 15,17), as discussed earlier. Eggert, Goettel and Silvera (Ref. 58) studied the real part of the dielectric constant of hydrogen in the visible frequency range at high pressures up to 73 GPa and proposed that these results presented indirect evidence of the metallic nature of the H-A phase. The physical objective was to measure the electronic band gap absorption and show that the gap goes to zero with metallization. This is difficult to measure in a DAC because diamonds strongly absorb above about 5 eV and the gap is 10-15 eV for low to moderately high pressure. However, one can relate the real and imaginary parts of the dielectric constant

and, from the behavior of the real part in the accessible visible part of the spectrum, infer the behavior of the absorptive part of the dielectric constant as a function of pressure. For hydrogen this is complicated because the band gap closure for metallization is expected to be indirect, resulting in a weak second-order process for absorption of radiation. In this case, the real part of the dielectric constant will be controlled much more strongly by the closure of the direct gap, which will happen at pressures substantially higher than the pressure for metallization. Thus such experiments should predict closure of the direct gap, and theory of the electronic structure must be used to imply when the indirect gap closes. Such measurements could at best give very weak indirect evidence of metallization. Hemley, Hanfland, and Mao (Ref. 59) extended these types of measurements to 170 GPa and still saw no evidence of direct band gap closure.

Mao, Hemley, and Hanfland (MHH) (Ref. 60) then measured the IR reflectance of hydrogen to pressures of 176 GPa at room temperature. Their spectral range had a long wavelength limit of about 2 microns. They reported that above about 150 GPa there was a rising edge in the reflectance at their long wavelength limit and that this edge moved to higher frequencies with increasing pressure. They presented values of the Drude parameters: the plasma frequency, the relaxation time, and the real part of the dielectric constant. They claimed that this provided the direct proof that the A-phase was the metallic molecular phase.

At the same time Eggert, et al (Ref. 61) also studied hydrogen by IR absorption and reflection to 230 GPa from 77 K to room temperature. Their long wavelength limit was 1.7 microns, slightly smaller than Mao, et al's range. They found no evidence of a Drude edge in either reflection or absorption. Even though their wavelength did not extend as low as that of Mao, et al, their pressure range was substantially higher and an extrapolation of the Drude parameters of Mao, et al indicated that their sample should have been strongly absorbing at pressures of 230 GPa. They noted that the data of Mao, et al, was not self-consistent. The Drude absorption and reflection are easily related. Mao, et al measured reflection in a DAC with parallel diamond culets and, as a consequence, interference fringes could be seen because of the Fabry-Perot cavity formed by the diamonds and the hydrogen (only when the index of hydrogen is equal to that of diamond at 130 GPa does the fringe contrast go to zero). However, for a sample with sufficient absorption the fringes should disappear as the multiplied reflected rays that lead to interference are attenuated.

Eggert, et al showed that in the sample of Mao, Hemley and Hanfland, fringes should be suppressed because of the absorption, based on their Drude parameters. Most of Mao, et al's samples were very rich in a powder of ruby, which was used to measure the pressure. Ruoff and Vanderborgh (Ref. 62) suggested that their ruby (Al_2O_3:Cr^{+++})may have been reduced to elemental Al, which could be responsible for their observations. Later it was found that this process would not take place at the 150 GPa level (Ref. 63). Ruoff (Ref. 64) also proposed that the observed edge might be caused by reflection from the combination of hydrogen and finely powdered ruby.

The next step in this development was an article by Hanfland, Hemley, and Mao (Ref. 65) who measured the IR absorption in hydrogen to pressures of 172 GPa at room temperature. They found a rising absorption edge, again at the 2-micron limit, as shown in Figure 8 by the open circles, squares, and triangles. This absorption strength was much weaker than would be predicted by their earlier Drude model. To have consistency with both reflection and absorption data, Hanfland, et al modified the numerical values of the index of refraction of hydrogen and diamond, important in the data analyses, and arrived at an entirely new set of Drude parameters in claiming that hydrogen was metallic. They used a value of the index of diamond greater than that of hydrogen in the region of metallization (pressures greater than 150 GPa).

Silvera (Ref. 66) analyzed this and showed that such a choice of index was unphysical, thus providing data that the model supporting the claim of metallization of hydrogen was flawed. At zero pressure, diamond has an index of refraction of about 2.4, while that of hydrogen is 1.15. With increasing pressure the index of diamond actually decreases, as discussed theoretically by Surh, Louie, and Cohen

16

(Ref. 67); by contrast, the index of hydrogen increases rapidly with the density. It is known from index matching that the two indices are equal at about 130 GPa (Ref. 59).

Since there are no severe changes of diamond or hydrogen with increasing pressure, the index of hydrogen must be higher than that of diamond in the 150-200 GPa region, after the crossing. Ruoff (Ref. 64) also argued along similar lines and refuted the claim by Mao, Hemley and Hanfland (Ref. 60). Nevertheless, the index of refraction of hydrogen has not been measured in the megabar region and the above discussion is one of the important reasons for the current effort to measure this quantity.
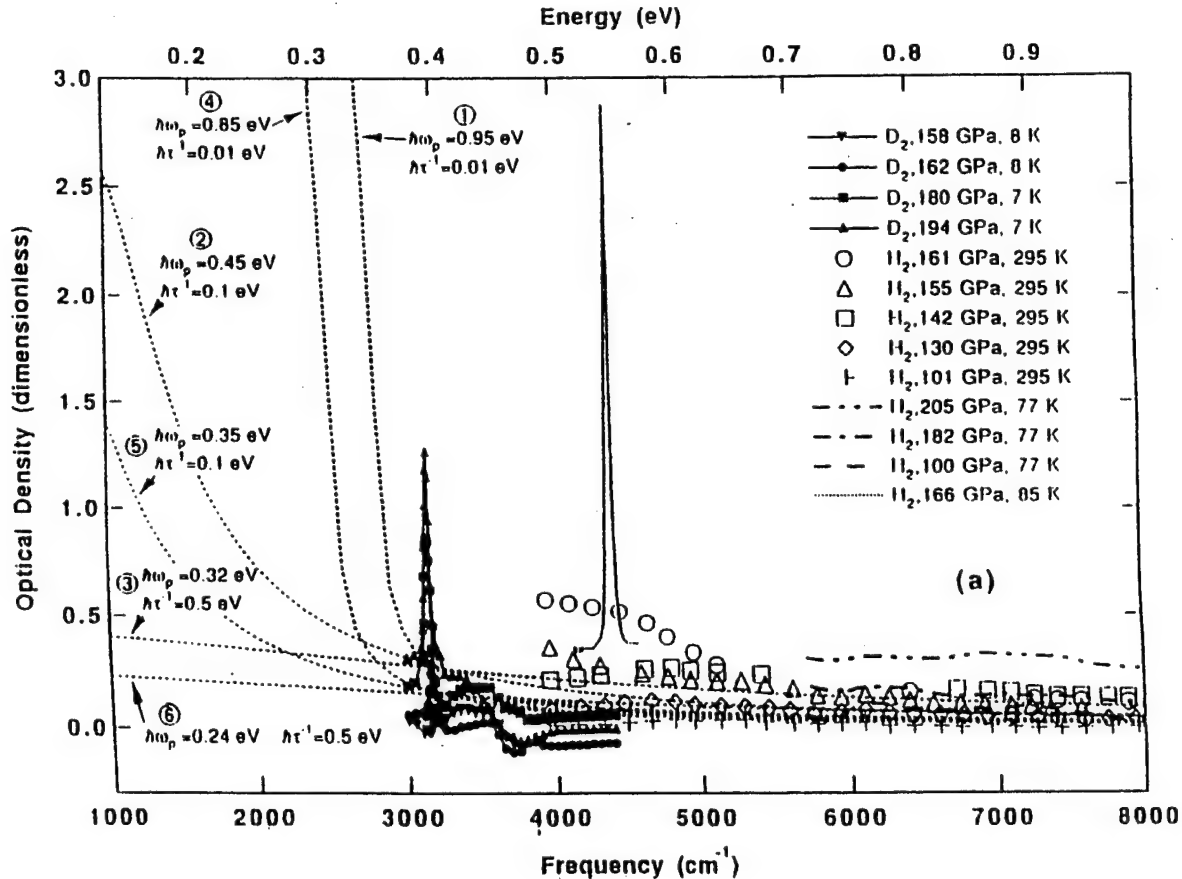

Figure 8
IR Absorption data in Spectra in Hydrogen and Deuterium

Subsequently there have been no further claims that the A-phases are metallic, although it is still suspected that they might be. A proof would require either a measurement of the electrical conductivity or an extension of the Drude measurements to a lower energy.

Recently, the IR absorption of solid deuterium at helium temperatures in a wavelength range that extends beyond the earlier long wavelength limit of 2.5 microns was measured (Ref. 30). To do this, a spectroscopic system in which a Burleigh color center laser could be swept in wavelength out to 3.3 microns was developed. Samples of deuterium pressurized up to 200 GPa were studied for their Drude behavior. The samples could be cooled down to liquid helium temperatures in a cryostat and allowed to convert to essentially 100% ortho-D_2 or could be studied at elevated temperatures and in various ortho-para mixtures. The results shown in Figure 9 show that absorption may be increasing as expected for a Drude metal at the higher pressures, but requires lower energies for a confirmation. This effect was found to be

17

more pronounced for measurements on pure o-D_2 than for mixed ortho-para crystals, implying that the spectrum is affected by this type of impurity effect, which could support the idea that mixed ortho-para crystals lead to Anderson localization. In Figure 8, a compilation of all broadband spectra measured on hydrogen or deuterium, to date, is shown. The dashed lines show Drude type behavior for various model parameters of a metal which would fit the data. However, the data only shows a slowly rising behavior. To answer the question of the metallic nature of the A-phase, the spectra must be extended to longer wavelengths.
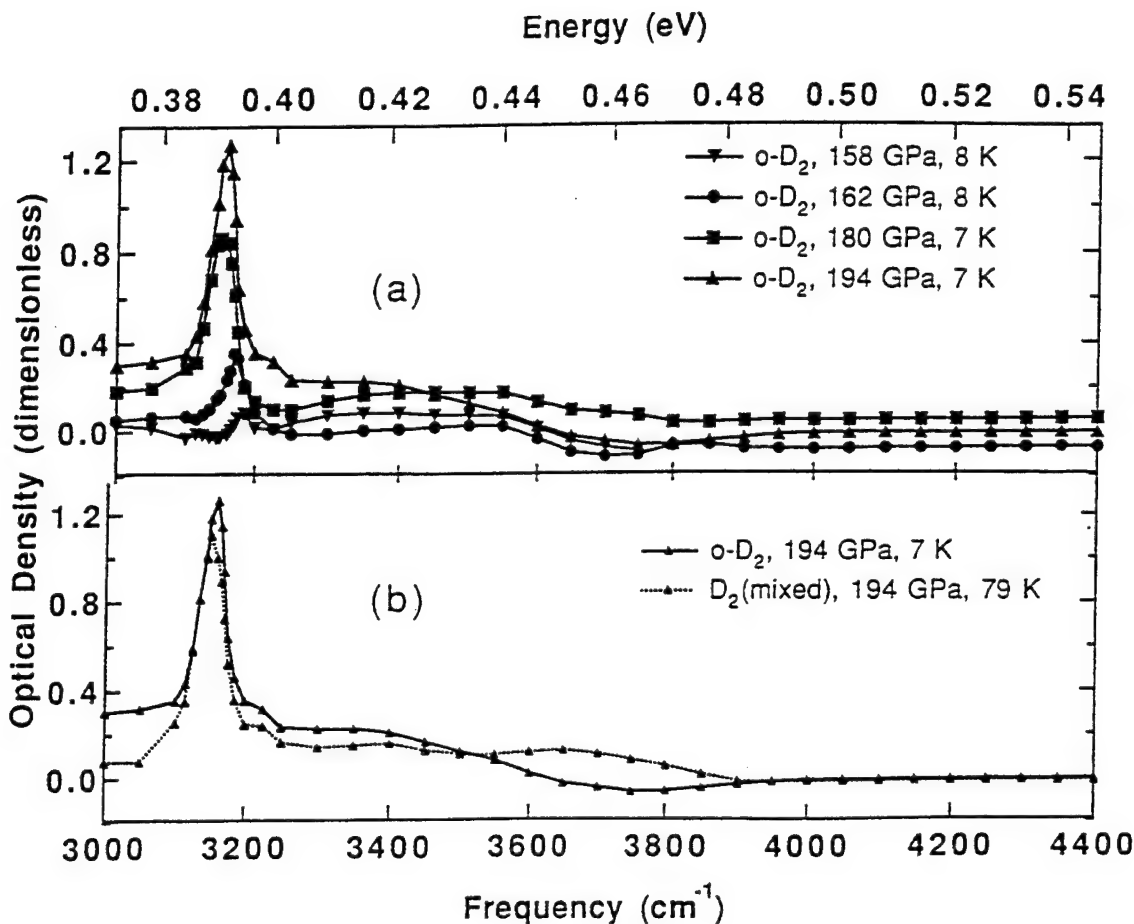

Figure 9
IR Absorption Spectra in Deuterium

To extend the spectroscopic measurements to wavelengths longer than 3.3 microns, a new optical system that uses a hot incandescent source for the radiation, instead of laser radiation, was developed. The source is a carbon tube, ohmically heated to about 2500 K, which produces substantially more radiant energy than the usual IR source (globar) that operates at about 1300 K. Three large Schwartzchild objectives to collect and focus light, which first passes through a grating monochromator, then through the DAC and onto the detector, were built. A reference arm for normalizing and stabilizing the power from the source was also built. The system, which is currently being automated, was designed to work to just less than 10 microns. In Figure 10, spectra that have been measured of type I and type II diamonds

demonstrating the performance of the instrument is shown. Unfortunately, in two high pressure runs, both sets of diamonds broke at megabar pressures, but under the pressure of 150 GPa needed for the A-phase of hydrogen.
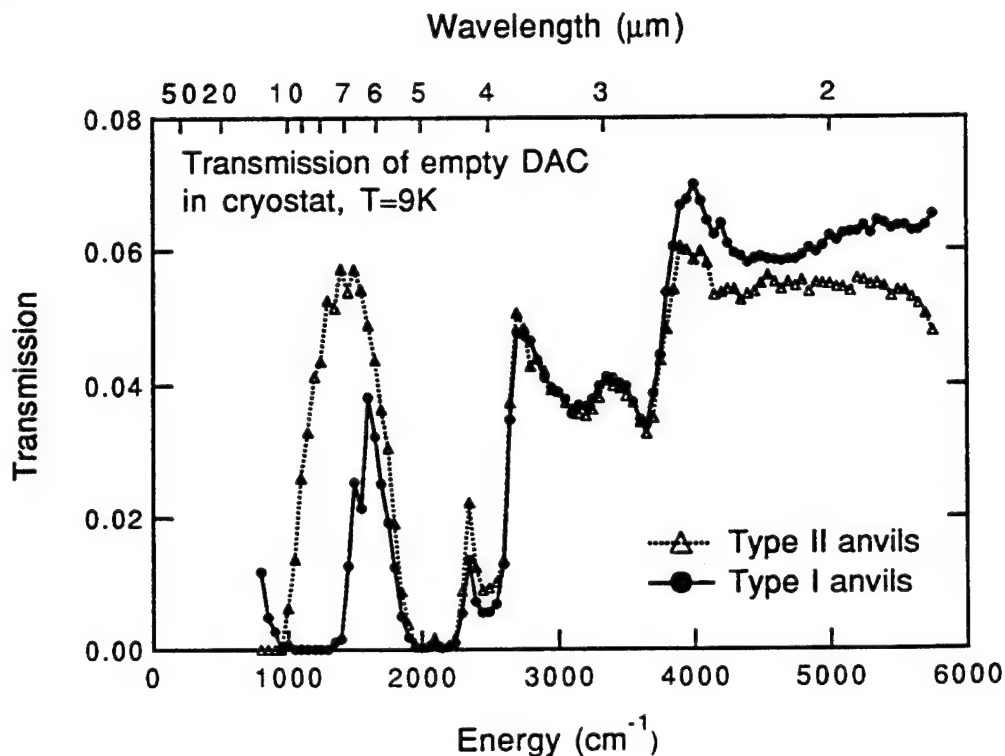

Figure 10
IR Transmission of Type I and IIA Diamonds

Other important phenomena concerning the A-phase exist. A critical point in the phase line separating the low pressure region from the H-A in a P-T plot was reported by Hemley and Mao (Ref. 68), as well as Lorenzana, Silvera, and Goettel (Ref. 69), indicated in Figure 7. The critical point was based on the observation that with increasing pressure the discontinuity in the vibron frequency at the phase transition went to zero. That critical point has very interesting consequences. As discussed by Silvera (Ref. 1), in traversing from the low pressure to the high pressure phase a thermodynamic path can be followed around the critical point. Thus the symmetry of the two phases must be the same, since a phase line was not crossed. Because the low pressure phase has hcp symmetry, this would imply that the H-A phase also has hcp symmetry. Such an important conclusion requires a closer examination of the evidence for a critical point.

Hanfland, Hemley, and Mao (Ref. 70) observed an infrared active vibron in the H-A phase, shown by the sharp peak at about 4500 cm^{-1}. Zallen, Martin, and Natoli (Ref. 71) pointed out that infrared activity was not allowed in the hcp lattice. However, such arguments are only valid for crystals with translational symmetry, and Hanfland, et al studied a mixed ortho-para crystal that lacks this symmetry. Cui, et al (Ref. 57) then studied a crystal of deuterium at low temperature, allowing it to convert to pure o-D$_2$ that does have translational symmetry; they observed an IR vibron in the D-A phase. Moreover, they determined the phase line between the low pressure (LP) phase and the BSP, as well as between the BSP and the A-phase, shown in Figure 1. They found that these lines converged at a triple point and the discontinuity in the Raman vibron disappeared in this region. Above this point a phase line exists between the D-A and the

LP phase so that there is no critical point, leading to the conclusion that the point identified as a critical point in hydrogen does not exist, as in deuterium. Thus, since the D-A and, presumably the H-A phases, have IR activity, the structure of the A-phase is not hcp-c because it does not have an IR active vibron mode; other structures such as the Pa3 can also be eliminated, based on these observations.

In this contract period an extensive study of the IR active and Raman active modes of the hydrogens was studied. Using group theoretical techniques and based on theoretical models, it is possible to further qualify or eliminate structures that have been proposed for the hydrogens. A compilation of the results of this study is shown in Table. I. The Raman and IR activity of various modes, compared to the experiments, are shown. In this way, a number of proposed structures such as hcp and Pa3 be eliminated, but can be identified, and the possible structures that can satisfy the observed spectra can be identified. One of the promising proposed structures was P2/m (Fig. 3). To further test this structure, the order parameter for the transition in crossing the line to the hcp phase (Fig. 11) was measured. Using the Landau theory and group theory one can show that the transition must be first order. However, it was observed that this is a second-order transition. As a result, the promising P2/m structure has been eliminated as one of the contenders.

Table 1. Group Theoretically Allowed Lattice Modes in the Hydrogens

Space Group	IR Vibron	Raman Vibron	IR Phonon	Raman Phonon
P6$_3$/mmc hcp-c	(0)	A$_{1g}$ (1)	(0)	E$_{2g}$ (1)
Pa3	(0)	A$_g$+T$_g$ (2)	2T$_u$ (2)	(0)
P4$_2$/mnm rutile	(0)	A$_{1g}$+B$_{1g}$* (2)	E$_u$ (1)	(0)
Pca2$_1$	A$_1$+B$_1$+B$_2$ (3)	A$_1$+A$_2$+B$_1$+B$_2$ (4)	2A$_1$+2B$_1$+2B$_2$ (6)	2A$_1$+3A$_2$+2B$_1$+2B$_2$ (9)
P2$_1$/c	A$_u$+B$_u$ (2)	A$_g$+B$_g$ (2)	2A$_u$+B$_u$ (3)	3A$_g$+3B$_g$ (6)
Pmc2$_1$	A$_1$+B$_1$* (2)	A$_1$+B$_1$* (2)	A$_1$+B$_1$* (2)	A$_1$+A$_2$+B$_1$* (3)
P2/m	B$_u$ (1)	A$_g$ (1)	(0)	2A$_g$+B$_g$ (3)
Cmca	(0)	A$_{1g}$+B$_{3g}$ (2)	B$_{1u}$+B$_{2u}$ (2)	(0)
P6$_3$/m	E$_{1u}$ (1)	2A$_g$+E$_{2g}$ (3)	A$_u$+2E$_{1u}$ (3)	2A$_g$+E$_{1g}$+3E$_{2g}$ (6)

Experimental Observations for ortho-D$_2$

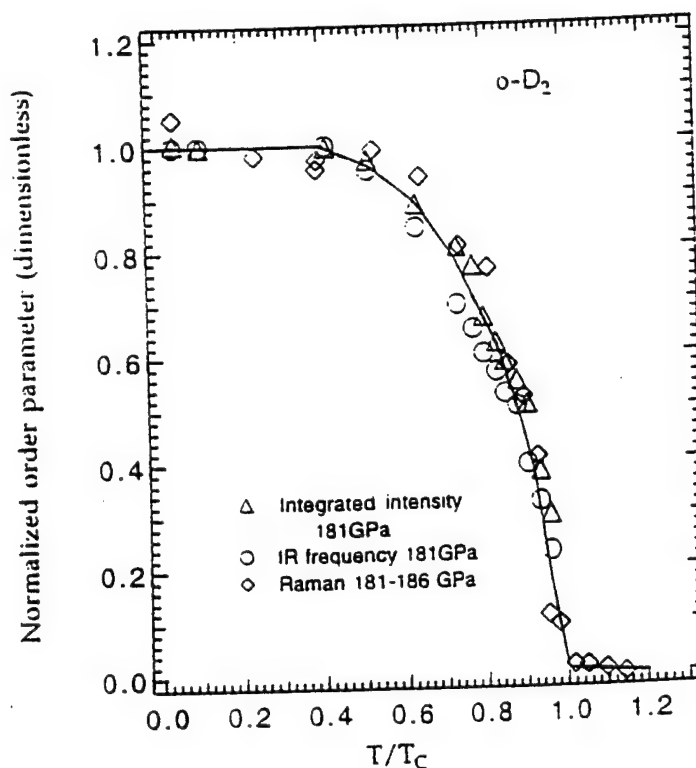|				
LP	0	1	--	
BSP	3	1	--	
D-A	1	1	--	

Figure 11
The Order Parameter in Deuterium

5.0 OTHER ACTIVITIES

In the current contract period research in a few other promising areas are reported on here. In this section the progress on measuring electrical conductivity and performing NMR on the hydrogens under high pressure is reported.

5.1. Electrical Conductivity

The most rigorous method of detecting metallization is to measure the dc electrical conductivity in the limit that the temperature goes to zero. The challenge of this technique is to design electrical leads that can be brought out from the high pressure region of the sample, through the gasket to ambient pressure. This is particularly difficult for hydrogen because the sample volume decreases by over an order of magnitude in pressurizing to 150 GPa and the deformation of the gasket generally leads to failure of the electrical leads. A number of innovative methods were tried out, but none of these yielded a result for pressures above 100 GPa. The most important of the various attempts is described here.

1. A gasket, as shown in Figure 12a, was built, requiring the development of construction techniques and a large amount of effort. This gasket consists of two Re sides separated by a Kapton (plastic insulator) layer. The Kapton fails at high pressure so the central region is filled with compressed alumina (Al_2O_3). A hole is then made in the center where the hydrogen sample is to be loaded, utilizing electric discharge machining (EDM). In this configuration a two-wire conductivity measurement can be made with each half of the gasket being an electrode. The gasket achieved 27 GPa before failure. The

21

failure was due to the Kapton/alumina extruding into the hole so that the sample lost its integrity or identity.

The next modification was to use e-beam sputtering to deposit a thick, denser layer of alumina. This was designed to prevent the extrusion of the alumina. This failed at 9 GPa. The alumina was brittle and cracked, leading to shorting and pieces falling into the central hole.

2. The next approach was to use an Re gasket with insulation on its surfaces and metallic conductors deposited on the diamonds, as shown in Figure 12b. The metallic coating was a 25Å Zr film, covered with a 17Å Cr film. The Zr makes a good bond to the diamond, which has to be carefully cleaned in acid (Ref. 72) and then sputter etched under vacuum to form a hard coating. The Cr coating protects the Zr from oxidizing or forming a hydride. The metallic film is separated into four pie-shaped, isolated sectors by means of a mask made of two crossed wires. The 2.5-micron thick film of alumina was applied by e-beam evaporation. The gasket shorted at 10.3 GPa and the hole filled with insulator.

3. A gasket with a dense core compressed into place, as shown in Figure 12c, was then constructed. The problem of the core material extruding or falling into the sample region is probably due to the high compressibility of the hydrogen sample at low pressure so that the brittle core undergoes extreme deformation. An ideal core would be more elastic or deformable at low pressure and very hard at high pressure. To achieve this a core of 3:1 mixtures (by volume) of alumna and C60 was made. Earlier research (Ref. 73) had shown that C60 is soft at low pressure, but in the 20-30 GPa region it transforms to a very hard form called collapsed fullerite. Although this seems to solve the materials problem, the core shown in Figure 12c did not adhere sufficiently well to the Re gasket and would fall out during drilling of the central hole for the sample.

The design was then modified to be similar to van Stratten and Silveras' (Ref. 72), which employed an all insulating core, as shown in Figure 12d.

In the first measurement the hole closed up during the hydrogen loading procedure. This was probably due to poor visibility of the sample region during cryogenic loading. In constructing the experiment, there was great difficulty getting the metallic coatings to adhere to the diamond. Extensive sputter cleaning resulted in surface damage to the culets, preventing good microscopy which is important for the loading. The usual interference spectroscopic technique could not be used to determine when the hydrogen was actually filling the gasket hole before applying the load. An empty gasket was put under load and the hole closed down.

The problems with coating were unusual and unexpected. Some years ago similar coatings had been made with little difficulty. This technique requires a very clean diamond surface before the deposition. A multi-user sputter system was used with inadequate access time because of the large number of users. It is possible that the UHV vacuum-jar was contaminated by other users, which poisoned the surfaces. To obtain a layer that adhered well, additional time was requested to thoroughly clean out the vacuum system (approximately four days of work). However, this type of access could not be obtained on a regular basis, which puts a severe boundary condition on the procedure that was used.

This experiment was repeated a second time, resulting in a good hard metallic coating. The usual electrode structure has four sectors for doing four-wire measurements. Up to 21 GPa was achieved with no shorting. In raising the pressure to 50 GPa a failure of a few of the electrodes happened, but measurements could still be made by using the gasket as an electrode. The sample accidentally warmed up to 200 K because of an overnight power failure in the building, which may have allowed hydrogen to diffuse into the diamonds, embrittling them. Following an additional increase of the pressure to approximately 80 GPa. the sample was lost. Opening of the cell revealed that one of the diamonds had failed.

One more attempt was made using the same method. In this case the electrodes started to peal off of the diamonds, away from the culet. The cracks in the electrodes were bridged with gold wire. This evidently dug into the alumina insulator and the sample leaked through this path during pressurization.

Several different configurations were tried without success. The most promising seemed to be the last one described. The greatest difficulty was attaching hard leads on the diamonds that do not peal off and

which can stand the large forces and abrasion during pressurization. The leads often abrade and open up at the sharp edges between facets of the diamonds. Because of the difficulty with getting a clean environment for deposition of the thin metallic films, this method was temporarily abandoned. Diamond culets are polished in-house to eliminate the sharp facets. This approach has promise for future success. Insulating cores with gold wires (or similar material) that pass from the sample to the outer low pressure region will be used in the future.
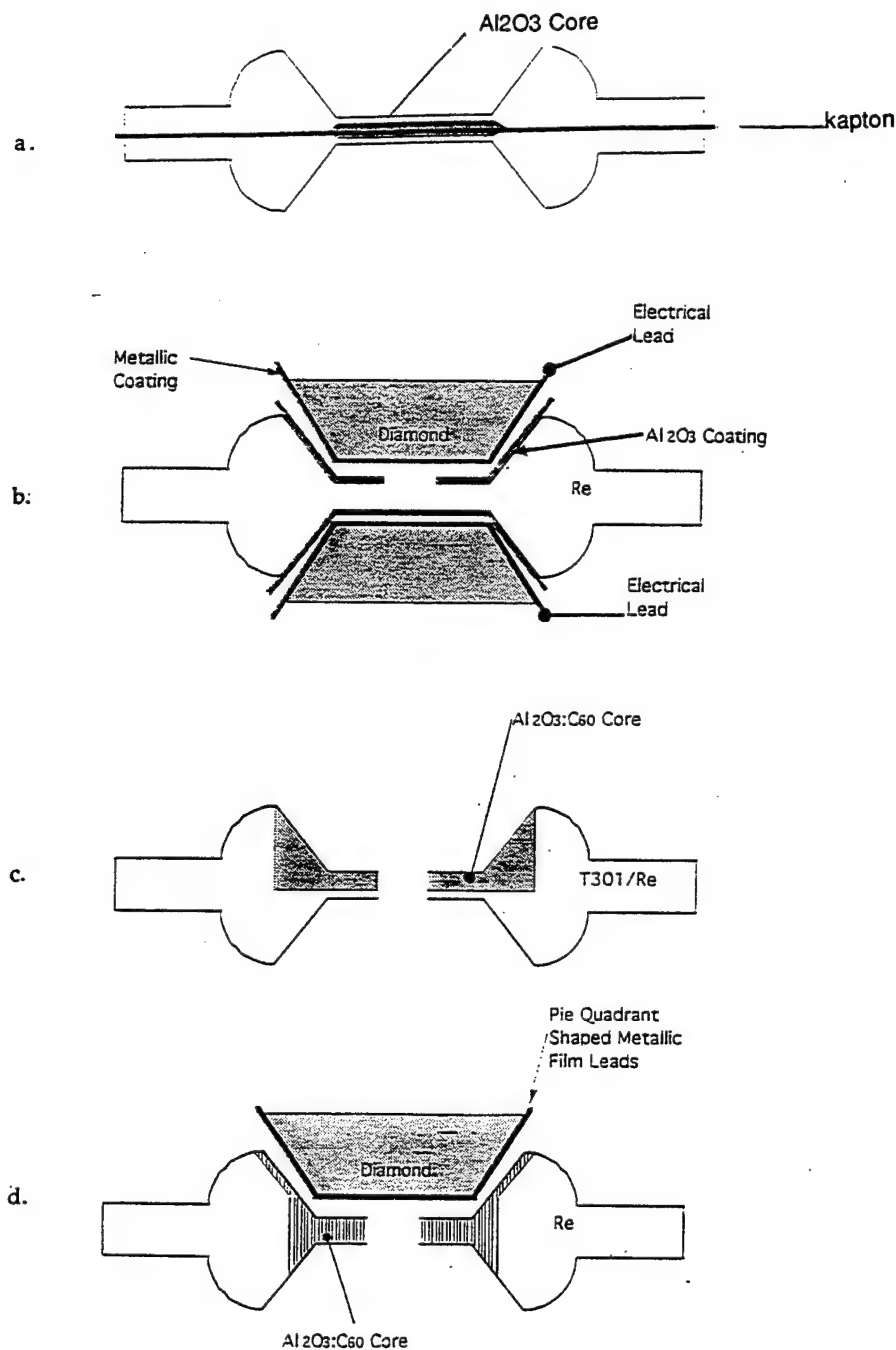

Figure 12
Gasket Designs for Electrical Conductivity in a DAC

5.2. NMR

In a second area, an NMR spectrometer for use with a DAC was developed. This pulsed spectrometer was built in-house and has been tested on both a gypsum sample at room temperature and a solid hydrogen sample at low temperature and ambient pressure. A free induction decay for the hydrogen sample is shown in Figure 13. After this test of the NMR system, experiments on hydrogen in a DAC were prepared. Since the NMR magnet cryostat does not have optical windows, the scheme was to load the sample by the usual cryogenic technique. By pressurizing the sample to greater than 5.4 GPa, it will remain solid at room temperature and not leak out. The DAC was transferred from the optical cryostat to the NMR cryostat. It is possible to raise or lower the pressure in-situ for studies of NMR as a function of pressure.
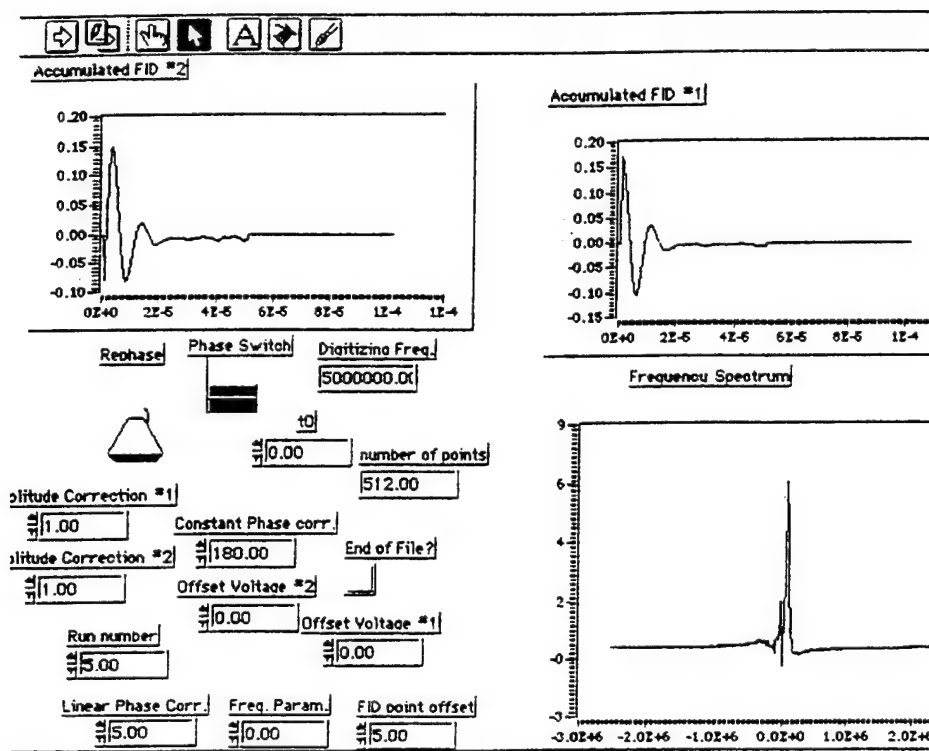

Figure 13
Free-Induction Decay of NMR in H₂

To measure the pressure using the ruby fluorescence from grains of ruby placed in the sample, a dual fiber optic system was built. One fiber carries laser light into the cryostat and, by means of a GRIN lens focuses onto the light on the sample to excite the fluorescence. A second graded index (GRIN) lens collects the fluorescence light, couples it to a fiber optic cable and carries the light to a spectrometer for analysis and determination of the pressure. A rugged system that maintains focus under varying circumstances was built. This is achieved by overfilling the sample at the sacrifice of some signal, which is not crucial because large ruby grains with large fluorescent signals can be used in NMR.

The next problem was to build a split gasket resonator, shown in Figure 14. Earlier NMR studies in DACs suffered from very small signals because of small filling factors (of order 10^{-3}). The problem is that the RF field is effectively shielded from penetrating into the sample by the gasket. In this most recent design, the gasket is split and forms a "hairpin" (single loop) coil, allowing the RF field into the sample

region through the slit, resulting in a large filling factor (a filling factor of about 0.5 was measured). To construct this gasket, a conventional gasket is drilled and a narrow slit is made with a wire EDM. The slit is then filled with a mixture of alumina and NaCl, which is heated to melt the NaCl and seal the gasket. (Experiments also consisted of putting an alumina and NaCl core in the center of the gasket, with a hole for the sample, as shown in Figure 14. This has the advantage of improved sealing of the sample because the sample does not "see" the discontinuity of the slit.) Ten to 20 percent Ag is added to enable EDM'ing of the sample hole. A gasket similar to the one in Figure 14 has been made and tested to 7 GPa using an alcohol/methanol mixture.
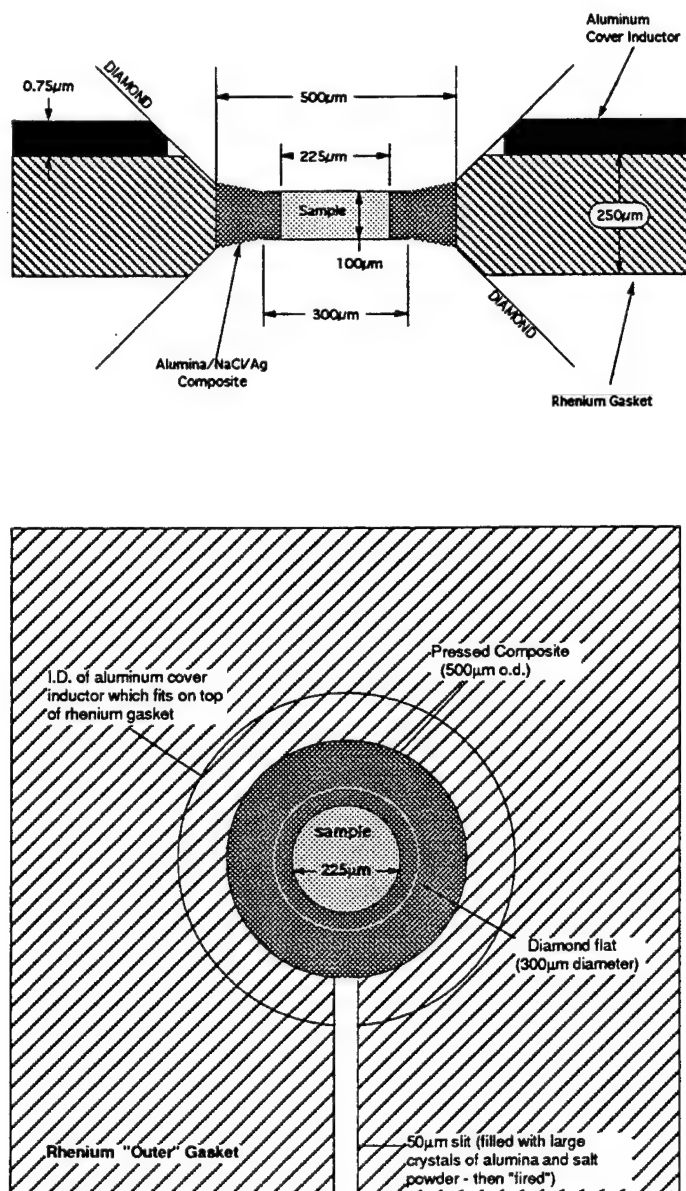

Figure 14
Gasket Design for NMR

The last part of the design is the coupling of the gasket to the NMR system. Originally, a capacitor was soldered to the gasket to make a resonator and a coax connected to this to couple the NMR pulse in and out. This turned out to be inefficient for two reasons. The Re gasket is optimized for the pressurization, but not for carrying RF currents. A higher Q cavity could be made if the gasket were made of Al, which has a lower impedance and a very small magneto-resistance. This problem is solved by putting a "cover" inductor of Al over the gasket so that this makes the resonant circuit and the RF field penetrates through the sample below. The second problem was poor coupling of the signal out of the sample. This was resolved by placing a half-wave coax between the circuit and a coupling capacitor to better match the RF signal back out of the circuit. All of this has been constructed in a Teflon chamber needed for loading the sample and sealing the coax, which passes from the sample out into the vacuum of the cryostat.

As of the writing of this report, two unsuccessful attempts have been made to observe NMR at high pressure. In the first, the hole in the cover gasket was too small and the gasket extruded into the sample hole during loading. In the second, after this problem was corrected, a sample was loaded successfully at 7 GPa. However, when warmed, the sample found a path to the outside and leaked out. It is believed that this problem was due to the discontinuity between the sample and the seal in the slit (this gasket did not have a central core). Very close to the sample the slit is highly deformed, and the asymmetry can lead to failure. To solve this problem a rather large core (300-400 micron diameter) is put around the 200-micron diameter sample. This is the actual design shown in Figure 14 Outside of this core the pressure is known to be very low, even when the sample is at a very high pressure. The sample will sit in a symmetric environment and the slit will not undergo severe deformation. Another advantage of this geometry is that it should be able to go to very high pressures, whereas the original design only worked up to about 10 GPa in preliminary tests at room temperature.

With these developments NMR experiments and plans to study ortho-para conversion and other problems shall be conducted in the future.

6.0 CONCLUSIONS AND RECOMMENDATIONS

In the past three years, substantial advances have been made in the understanding of hydrogen at ultra-high pressures. Efforts in this study have been concentrated on the lower megabar range (100-200 GPa) in an effort to understand the suspected metallic A-phase and other phases. Substantial progress has been made in determining the phase diagram. The earlier proposed critical point for hydrogen appears to have been misidentified and is more likely a triple point, as has been observed in deuterium. An understanding of the BSP phase has been refined, with the determination of the phase lines for both deuterium and HD. That of hydrogen still needs to be studied. The development of a tunable IR spectroscopic instrument enabled the study and determination of the phase diagram of IR active vibrons in deuterium. From this and the use of group theory, progress has been made in the effort to determine and understand the structure of the A-phases. Broad-band IR absorption experiments have been used to study the possibility of Drude behavior in deuterium, which would be evidence of metallization. These results indicate that it is important to extend the measurements to still longer wavelengths to characterize the conductive state of the hydrogens.

Advances in the pressurization and study of the hydrogens in the past three years, using diamond anvil cell techniques, have proceeded rapidly, yet there are still many uncertainties. Continued efforts to understand the A-phase should be undertaken, both spectroscopically and by measuring conductivity in hydrogen and its isotopes. Spectroscopic techniques for very long IR wavelengths should be further developed and used to study both the Drude nature and the excitation spectra of the high pressure solids. In particular, it is recommended that the conductive method be developed to work to multimegabar pressures and that efforts be made to extend the pressure range to 4-5 megabars to seek the metallic atomic state. Four terminal measurements will allow the determination of the superconductive nature of the metallic atomic hydrogen. The development of NMR should be pursued. In particular, a study of the ortho-para

content and ortho-para conversion rates at very high pressures is important to the understanding of the high-density properties and is related to the question of metallization. The NMR technique can also be used to study the intramolecular bond as a function of pressure and order-disorder phenomena.

7.0 REFERENCES

1. Silvera, I.F., "Implications Of The High Pressure Critical Point Of Hydrogen On The Structure of ohe H-A Phase," *Sov. J. Low Temp. Phys.*, **19,** 1993, pp. 628-630.

2. Mott, N.F., *Proc. Phys. Soc.*, **A62,** 1949, pp. 416-422.

3. Wigner, E. and H.B. Huntington, "On the Possibility of a Metallic Modification of Hydrogen," *J. Chem. Phys.*, **3,** 1935, pp. 764-770.

4. Kronig, R., J.D. Boer, and J. Korringa, "On the Internal Constitution of the Earth," *Physica XII,* 1946, pp. 245-255.

5. DeMarcus, W.C., "The Constitution of Jupiter and Saturn," *The Astronomical Journ.*, **63,** 1958, pp. 2-28.

6. Ashcroft, N.W., "Metallic Hydrogen: A High Temperature Superconductor?" *Phys. Rev. Lett.*, **21,** 1968, pp. 1748-1749.

7. Brovman, E.G., Y. Kagan, and A. Kholas, "Structure of Metallic Hydrogen at Zero Pressure," *Sov. Phys. JETP*, **34,** 1972, pp. 1300-1315.

8. Salpeter, E.E., "Evaporation of Cold Metallic Hydrogen," *Phys. Rev. Lett.*, **28,** 1972, pp. 560-562.

9. Ramaker, D.E., L. Kumar, and F.E. Harris, "Exact-Exchange Crystal Hartree-Fock Calculations of Molecular and Metallic Hydrogen and Their Transitions," *Phys. Rev. Lett.*, **34,** 1975, pp. 812-814.

10. Friedli, C. and N.W. Ashcroft, "Combined Representation Method for Use in Band-Structure Calculations: Application to Highly Compressed Hydrogen," *Phys. Rev. B*, **16,** 1977, pp. 662-672.

11. Ceperley, D.M. and B.J. Alder, "The Ground State of Solid Hydrogen at High Pressures," *Phys. Rev. B*, **36,** 1987, pp. 2092-2106.

12. Natoli, V., R.M. Martin, and D. Ceperley, "Crystal Structure of Molecular Hydrogen at High Pressure," *Phys. Rev. Lett.*, **74,** 1995, pp. 1601-1605.

13. Cohen, M.L., "Predicting New Solids and Superconductors," *Science*, **234,** 1986, pp. 549-553.

14. Barbee, T.W., III, et al., "Theory of High-Pressure Phases of Hydrogen," *Phys. Rev. Lett.*, **62,** 1989, pp. 1150-1153.

15. Garcia, A., et al., "Bandgap Closure and Metallization of Molecular Solid Hydrogen," *Europhysics Lett.*, **13,** 1990, pp. 355-360.

16. Ashcroft, N.W., "Pairing Instabilities in Dense Hydrogen," *Physical Review B*, **41,** 1990, pp. 10963-10971.

17. Chacham, H. and S.G. Louie, "Metallization of Solid Hydrogen at Megabar Pressures: A First Principles Quasiparticle Study," *Phys. Rev. Lett.*, **66,** 1991, pp. 64-68.

18. Kaxiras, E., J. Broughton, and R.J. Hemley, "Onset of Metallization and Related Transitions in Solid Hydrogen, " *Phys. Rev. Lett.*, **67,** 1991, pp. 1138-1141.

19. Kaxiras, E. and J. Broughton, "Energetics of Ordered Structures in Molecular Hydrogen" *Europhys. Lett.*, **17,** 1992, pp. 151-155.

20. Cui, L., N.H. Chen, and I.F. Silvera, "Excitations, Order Parameters, and Phase Diagram of Solid Deuterium at Megabar Pressures," *Phys. Rev. B*, **51,** 1995, pp. 14987-97.

21. Nagara, H. and T. Nakamura, "Stable Phases of Solid Hydrogen at Megabar Pressures and at Zero Temperature," *Physical Review Letters*, **68,** 1992, pp. 2468-2471.

22. Surh, M.P., T.W. Barbee, and C. Mailhiot, "Zero-Point Motion and the Insulator-Metal Transition in Solid Molecular Hydrogen" *Phys. Rev. Lett.*, **70,** 1993, pp. 4090-4094.

23. Edwards, B. and N.W. Ashcroft, "The Structure of Hydrogen Near the 150GPa Transition," *Bull. Am. Phys. Soc.*, **39,** 1994, pp. 336.

24. Ashcroft, N.W., "The Metal Insulator Transition: Complexity in a Simple System," *Journal of Non-crystalline Solids*, **156,** 1993, pp. 621-630.

25. Brovman, E.G., Y. Kagan, and A. Kholas, "Properties of Metallic Hydrogen under Pressure," *Sov. Phys. JETP*, 1972, pp. 783-787.

26. Mon, K.K., G.V. Chester, and N.W. Ashcroft, "Simulation Studies of a Model of High Density Metallic Hydrogen," *Phys. Rev. B*, **21,** 1980, pp. 2641-2646.

27. Oliva, J. and N.W. Ashcroft, "Two-Component Fermi-Liquid Theory: Equilibrium Properties of Liquid Metallic Hydrogen," *Phys. Rev. B*, **23,** 1981, pp. 6399-6407.

28. Oliva, J. and N.W. Ashcroft, "Theory of the Spin-1 Bosonic Liquid Metal: Equilibrium Properties of Liquid Metallic Deuterium," *Phys. Rev. B*, **30,** 1984, pp. 1326-1335.

29. Natoli, V., R.M. Martin, and D.M. Ceperley, "Crystal Structure of Atomic Hydrogen," *Phys. Rev. Lett.*, **70,** 1993, pp. 1952-1955.

30. Cui, L., N.H. Chen, and I.F. Silvera, "Infrared Properties of Ortho and Mixed Crystals of Solid Deuterium at Megabar Pressures and the Question of Metallization in the Hydrogens," *Phys. Rev. Lett.*, **74,** 1995, pp. 4011-4014.

31. Barbee, T.W., A. García, and M.L. Cohen, "First-Principles Prediction of High-Temperature Superconductivity in Metallic Hydrogen" *Nature*, **340,** 1989, pp. 369-371.

32. Silvera, I.F., "The Solid Molecular Hydrogens in the Condensed Phase: Fundamentals and Static Properties," *Rev. Mod. Phys.*, **52**, 1980, pp. 393-452.

33. Driessen, A. and I.F. Silvera, "Ortho-para Conversion of Solid Hydrogen as a Function of Density," *Phys. Rev. B*, **30**, 1984, pp. 2517-2526.

34. Driessen, A. and I.F. Silvera, "An Improved Experimental Equation of State of Solid Hydrogen and Deuterium," *J. Low Temp. Physics*, **54**, 1984, pp. 361-395.

35. van Straaten, J. and I.F. Silvera, "Equation of State of Solid Molecular H2 and D2 at 5 Kelvin," *Phys. Rev. B*, **37**, 1988, pp. 1989-2000.

36. Shimizu, H., et al., "Brillouin Measurements of Solid n-H2 and n-D2 to 200 kbar at Room Temperature," *Phys. Rev. Lett.*, **47**, 1981, pp. 128-131.

37. Shimizu, H. and T. Kumazawa, "Equation of State for Fluid Hydrogen-Isotopes H2, D2, and T2 up to Their Freezing Points at 300 K," *J. Chem. Phys.*, **78**, 1983, pp. 4632-4636.

38. Zha, C., et al., "Elasticity of Hydrogen to 24 Gpa from Single Crystal Brillouin Scattering and Synchrotron X-Ray Diffraction," *Phys. Rev. B*, **48**, 1993, pp. 9246-9255.

39. Hemley, R.J., et al., "Equation of State of Solid Hydrogen and Deuterium from Single-Crystal X-Ray Diffraction to 26.5 GPa," *Phys. Rev. B*, **42**, 1990, pp. 6458-6470.

40. Ishmaev, S.N., et al., "Neutron Structural Investigations of Solid Parahydrogen at Pressures Up to 24 Kbar," *Sov. Phys. JETP*, **57**, 1983, pp. 228-233.

41. Glazkov, V.P., et al., "Neutron Diffraction of Deuterium to 30.9 GPa," *Pis'ma. Zh. Eksp. Teor. Fiz*, **47**, 1988, pp. 661-665.

42. Silvera, I.F. and R. Jochemsen, "Orientational Ordering in Solid Hydrogen: Dependence of Critical Temperature and Concentration on Density," *Phys. Rev. Lett.*, **43**, 1979, pp. 337.

43. Raich, J.C. and R.D. Etters, "Rotational Motion Under Pressure in the Solid Molecular Hydrogen Isotopes," *J. Low Temp. Phys.*, **22**, 1972, pp. 213-222.

44. Lagendijk, A. and I.F. Silvera, "Roton Softening in the Solid Hydrogen," *Phys. Letters*, **84A**, 1981, pp. 28-31.

45. Silvera, I.F. and R.J. Wijngaarden, "New Low Temperature Phase of Molecular Deuterium at Ultra High Pressure," *Phys. Rev. Lett.*, **47**, 1981, pp. 39-42.

46. Lorenzana, H.E., I.F. Silvera, and K.A. Goettel, "Orientational Phase Transitions in Hydrogen at Megabar Pressures," *Phys. Rev. Lett.*, **64**, 1990, pp. 1939-1942.

47. Moshary, F., N.H. Chen, and I.F. Silvera, "Remarkable High Pressure Phase Line of Orientational Order in Solid Hydrogen Deuteride," *Phys. Rev. Lett.*, **71**, 1993, pp. 3814-3817.

48. Grigor'ev, F.V., et al., "Experimental Determination of the Compressibility of Hydrogen at Densities 0.5-2 g/cm3. Metallization of Hydrogen," *JETP Lett.*, **16**, 1972, pp. 201-204.

49. Kawai, N., M. Togaya, and O. Mishima, "Experimental Metallization of Hydrogen," *Proc. of the Japan Academy*, **51**, 1975, pp. 630-633.

50. Vereshchagin, L.F., E.N. Yakovlev, and Y.A. Timofeev, "Possibility of Transition of Hyudrogen into the Metallic State," *JETP Lett.*, **21**, 1975, pp. 85-86.

51. Hawke, R.S., et al., "Observation of Electrical Conductivity of Isentropically Compresssed Hydrogen at Megabar Pressures," *Phys. Rev. Lett.*, **41**, 1978, pp. 994-998.

52. Mao, H.K. and R.J. Hemley, "Optical Studies of Hydrogen above 200 Gigapascals: Evidence for Metallization by Band Overlap," *Science*, **244**, 1989, pp. 1462-1465.

53. Silvera, I.F., "Evidence for Band Overlap Metallization of Hydrogen," *Science*, **247**, 1990, pp. 863-864.

54. Hemley, R.J. and H.K. Mao, "Phase Transitions in Solid Molecular Hydrogen at Ultrahigh Pressures," *Phys. Rev. Lett.*, **61**, 1988, pp. 857-860.

55. Lorenzana, H.E., I.F. Silvera, and K.A. Goettel, "Evidence for a Structural Phase Transition in Solid Hydrogen at Megabar Pressures," *Phys. Rev. Lett.*, **63**, 1989, pp. 2080-2083.

56. Hemley, R.J. and H.K. Mao, "Isotope Effects in Dense Solid Hydrogen: Phase Transition in Deuterium at 190(±20) GPa," *Phys. Rev. Lett.*, **63**, 1989, pp. 1393-1395.

57. Cui, L., et al., "Megabar Pressure Triple Point in Solid Deuterium," *Phys. Rev. Lett.*, **72**, 1994, pp. 3048-3051.

58. Eggert, J.H., K.A. Goettel, and I.F. Silvera, "High Pressure Dielectric Catastrophe and the Possibility that the Hydrogen-A Phase is Metallic," *Europhys. Lett.*, **11**, 1990, pp. 775-781.

59. Hemley, R.J., M. Hanfland, and H.K. Mao, "High Pressure Dielectric Measurements of Solid Hydrogen to 170 GPa," *Nature*, **350**, 1991, pp. 488-91.

60. Mao, H.K., R.J. Hemley, and M. Hanfland, "Infrared Reflectance Measurements of the Insulator-Metal Transition in Solid Hydrogen," *Phys. Rev. Lett.*, **65**, 1990, pp. 484-487.

61. Eggert, J.H., et al., "Absorption and Reflectance in Hydrogen Up to 230 GPa: Implications for Metallization," *Phys. Rev. Lett.*, **66**, 1991, pp. 193-196.

62. Ruoff, A.L. and C.A. Vanderborgh, "Hydrogen Reduction of Ruby at High Pressure: Implication for Claims of Metallic Hydrogen," *Phys. Rev. Lett.*, **66**, 1991, pp. 754-757.

63. Greene, R.G., H. Luo, and R.L. Ruoff, "High Pressure Raman and EDXD Study of Diaspore," *High Pressure Science and Technology-1993*, S.C. Schmidt, et al., Editor. 1994, AIP Conf. Proc.: Colorado Springs, CO, p. 1535-1538.

64. Ruoff, A.L., "Implications of Experiments on Hydrogen," *High Pressure Science and Technology-1993*, S.C. Schmidt, et al., Editor. 1994, AIP: Colorado Springs, CO, p. 849-52.

65. Hanfland, M., R.J. Hemley, and H.K. Mao, "Optical Absorption Measurements of Hydrogen at Megabar Pressures," *Phys. Rev. B*, **43**, 1991, pp. 8767-8770.

66. Silvera, I.F., "Solid Hydrogen at Ultra High Pressure," *NATO ARW on Frontiers of High Pressure Research*, 1991. Plenum Press, New York, pp. 101-114

67. Surh, M.P., S.G. Louie, and M.L. Cohen, "Band Gaps of Diamond Under Anisotropic Stress," *Phys. Rev. B*, **45**, 1992, pp. 8239-8247.

68. Hemley, R.J. and H.K. Mao, "Critical Behavior in the Hydrogen Insulator-Metal Transition," *Science*, **249**, 1990, pp. 391-393.

69. Lorenzana, H.E., I.F. Silvera, and K.A. Goettel, "The Order Parameter and a Critical Point on the Megabar Pressure Hydrogen-A Phase Line," *Phys. Rev. Lett.*, **65**, 1990, pp. 1901-1904.

70. Hanfland, M., R.J. Hemley, and H.K. Mao, "Novel Infrared Vibron Absorption of Solid Hydrogen at Megabar Pressures," *Phys. Rev. Lett.*, **70**, 1993, pp. 3760-3763.

71. Zallen, R., R.N. Martin, and V. Natoli, "Infrared Activity in Elemental Crystals," *Physical Rev. B*, **49**, 1994, pp. 7032-7035.

72. van Straaten, J. and I.F. Silvera, "Electrical Resistance Measurements on Cryocrystals in a Diamond Anvil Cell to 70 GPa," *Rev. Sci. Instrum.*, **58**, 1987, pp. 994-996.

73. Moshary, F., et al., "Gap Reduction and the Collapse of Solid C60 to a New Phase of Carbon Under Pressure," *Phys. Rev. Lett.*, **69**, 1992, pp. 466-469.

PUBLICATIONS SUPPORTED BY CONTRACT F29601-92-K-0019

1. Silvera, I.F., "Pressing for Metallic Hydrogen," Proc. Finnish Physical Society Annual Meeting, (1992); Arkhimedes **2**, 108-125 (1992).

2. Moshary, F., Chen, N.H., Silvera, I.F., "Pressure Dependence of the Vibron in H_2, HD, and D_2 Implications for Inter- and Intramolecular Forces," *Phys. Rev. B* **48**, 12 613, (1993).

3. Silvera, I.F., Chen, N., Moshary, F., "Orientational Order in The Solid Hydrogens: The Boomerang Phase Line in HD," American Institute of Physics (AIP) Conf. Proc., **309**, Part 1 841-844 (1994).

4. Moshary, F., Chen, N., Silvera, I.F., "Remarkable High Pressure Phase Line of Orientational Order in Solid Hydrogen Deuteride," *Phys. Rev. Lett.* **71**, 3814 (1993).

5. Silvera, I.F., "Implications of the High Pressure Critical Point of Hydrogen on the Structure of the H-A Phase," *Sov. J. of Low Temp. Phys.*, **19**, (5), 628-630 (1993).

6. Cui, L., Chen, N.H., Jeon, S.J., Silvera, I.F., "Megabar Pressure Triple Point in Solid Deuterium," *Phys. Rev. Lett.* **72**, 3048-3051 (1994).

7. Cui, L., Chen, N.H., Silvera, I.F., "Infrared Properties of Ortho and Mixed Crystals of Solid Deuterium at Megabar Pressures and the Question of Metallization in the Hydrogens," *Phys. Rev. Lett.*, **74**, 4011 (1995).

8. Cui, L., Chen, N.H., Silvera, I.F., "Excitations, Order Parameters, and Phase Diagram of Solid Deuterium at Megabar Pressures," *Phys. Rev. Lett.*, **B51**, 14987 (1995).